Guidance Document

Validation of Chlorine and Oxygen Isotope Ratio Analysis
To Differentiate Perchlorate Sources and to Document
Perchlorate Biodegradation

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Perchlorate in the environment is derived from both synthetic and natural sources. Synthetic perchlorate salts have been widely used as oxidants by the military and aerospace industry. A variety of commercial products also contain synthetic perchlorate. In addition to synthetic sources, natural perchlorate from both Chilean fertilizers and indigenous sources represents a potentially large source of perchlorate in groundwater and drinking water in the U.S. The key objective of the isotopic techniques described in this guidance manual is to provide evidence concerning the origin of perchlorate in soils and groundwater, and more specifically whether that perchlorate is synthetic or natural. Chlorine and oxygen isotopic analyses of perchlorate provide the primary direct approach whereby different sources of perchlorate can be distinguished from each other. Other isotopic, chemical, and geochemical techniques that can be applied in conjunction with isotopic analyses of perchlorate to provide supporting data in forensic studies are also described.

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ACRONYMS AND ABBREVIATIONS

‰	per mil
δ, Δ	delta, relative difference of isotope ratios
Ag	silver
AgCl	silver chloride
$AgNO_3$	silver nitrate
Al	aluminum
AMS	accelerator mass spectrometry
Ar	argon
Ba	barium
$BaCl_2$	barium chloride
$BaSO_4$	barium sulfate
bgs	below ground surface
BOMARC	Boeing and Michigan Aerospace Research Center
Br^-	bromide
BV	bed volumes
°C	degrees Celsius
Ca	calcium
CFC	chlorofluorocarbon
CF-IRMS	continuous-flow isotope ratio mass spectrometry
CH_4	methane
CH_3Cl	methyl chloride
CH_3I	methyl iodide
Cl^-	chloride
Cl	chlorine
^{35}Cl	chlorine-35
^{36}Cl	chlorine-36
^{37}Cl	chlorine-37
ClO_3^-	chlorate
ClO_4^-	perchlorate
cm	centimeters
CO	carbon monoxide
CO_2	carbon dioxide
COC	chain-of-custody
CsCl	cesium chloride
$CsClO_4$	cesium perchlorate
CsOH	cesium hydroxide
CSIA	compound-specific stable isotope analysis
Cu	copper
DDI	distilled deionized (water)
DI	deionized (water)
DI-IRMS	dual-inlet isotope ratio mass spectrometry
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	Department of Defense

DTSC	Department of Toxic Substance Control
EIGL	Environmental Isotope Geochemistry Laboratory
ESTCP	Environmental Security Technology Certification Program
Fe	iron
Fe^{3+}	iron (III)
$FeCl_3$	iron (III) chloride or ferric chloride
$FeCl_4^-$	tetrachloroferrate
$Fe(OH)_3$	iron (III) hydroxide
g	gram
gal	gallon
GC	gas chromatograph
^3H	tritium
ha	hectare
HCl	hydrochloric acid
$HClO_4$	perchloric acid
HCO_3	bicarbonate
HDPE	high density polyethylene
He	helium
HNO_3	nitric acid
H_2O	water
H_2O_2	hydrogen peroxide
HPLC-UV	high performance liquid chromatography with ultraviolet detection
hr	hours
IAEA	International Atomic Energy Agency
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ID	inner diameter
IO_3^-	iodate
IRMS	isotope-ratio mass spectrometry
ITRC	Interstate Technology & Regulatory Council
IX	ion exchange
k	one thousand
K	potassium
KCl	potassium chloride
$KClO_4$	potassium perchlorate
kg	kilogram
km^2	square kilometer
KNO_3	potassium nitrate
KOH	potassium hydroxide
Kr	Krypton
kyr	thousand years
L	liter
LC-MS/MS	liquid chromatography-tandem mass spectrometry
μg	microgram
μg/L	microgram per liter
μm	micron

μmol	micromole
M	molar
m	meter
MΩ	megohm
MADEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
MDL	method detection limit
Mg	magnesium
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mM	millimolar
MRGB	Middle Rio Grande Basin
MTBE	methyl *tert*-butyl ether
Myr	million years
m/z	mass-to-charge ratio
n	amount of substance
N	nitrogen or normal or number of entities
N_2	nitrogen gas
Na	sodium
NaCl	sodium chloride
$NaClO_4$	sodium perchlorate
NADP	National Atmospheric Deposition Program
$NaNo_3$	sodium nitrate
NaOCl	sodium hypochlorite (bleach)
NaOH	sodium hydroxide
NASA	National Aeronautics and Space Administration
Ne	neon
ng	nanogram
NH_4ClO_4	ammonium perchlorate
NIST	National Institute of Standards and Technology
N_2O	nitrous oxide
NO_2^-	nitrite
NO_3^-	nitrate
NO_3-N	nitrate as nitrogen
NPT	National pipe thread
O	oxygen
^{16}O	oxygen-16
^{17}O	oxygen-17
^{18}O	oxygen-18
O_2	oxygen gas
O_3	ozone
OD	outer diameter
ORNL	Oak Ridge National Laboratory
ORP	oxidation-reduction potential

per mil (‰)	part per thousand ($\times 10^{-3}$)
ppb	part per billion ($\times 10^{-9}$)
ppm	part per million ($\times 10^{-6)}$
PO_4^{2-}	phosphate
PRIME	Purdue Rare Isotope Measurement Laboratory
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RbCl	rubidium chloride
$RbClO_4$	rubidium perchlorate
Re	rhenium
ReO_4^-	perrhenate
S	sulfur
Sb	antimony
SCWA	Suffolk County Water Authority
SERDP	Strategic Environmental Research and Development Program
SF_6	sulfur hexafluoride
SHP	Southern High Plains
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
SO_2	sulfur dioxide
SO_4^{2-}	sulfate
Sr	strontium
TcO_4^-	pertechnetate
UCMR	Unregulated Contaminant Monitoring Rule
UIC	University of Illinois at Chicago
U.S.	United States
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
VOCs	volatile organic compounds
VSMOW	Vienna Standard Mean Ocean Water
x	mole fraction
Xe	xenon
yr	year

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EXECUTIVE SUMMARY

Increased health concerns about perchlorate (ClO_4^-) during the past decade and subsequent regulatory considerations have generated appreciable interest in source identification. The key objective of the isotopic techniques described in this guidance manual is to provide evidence concerning the origin of ClO_4^- in soils and groundwater and, more specifically, whether that ClO_4^- is synthetic or natural. Chlorine and oxygen isotopic analyses of ClO_4^- provide the primary direct approach whereby different sources of ClO_4^- can be distinguished from each other. These techniques measure the relative abundances of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- using isotope-ratio mass spectrometry (IRMS). In addition, the relative abundance of the radioactive chlorine isotope ^{36}Cl is measured using accelerator mass spectrometry (AMS). Taken together, these measurements provide four independent quantities that can be used to distinguish natural and synthetic ClO_4^- sources, to discriminate different types of natural ClO_4^-, and to detect ClO_4^- biodegradation in the environment. Other isotopic, chemical, and geochemical techniques that can be applied in conjunction with isotopic analyses of ClO_4^- to provide supporting data in forensic studies are also described.

This guidance manual is intended to provide details of the methodology used to (1) collect ClO_4^- samples from the environment, particularly from groundwater, which is the main medium of interest for ClO_4^- source identification; (2) purify the collected ClO_4^- samples; (3) conduct oxygen (O) and chlorine (Cl) isotopic analyses on the purified samples; and (4) determine probable sources using the resulting isotope data. Current practices for groundwater sampling and quality assurance for sample collection, purification, and measurement of Cl and O isotopes in ClO_4^- are provided. A detailed case study of source evaluation in groundwater on Long Island is given along with the current literature on the subject of ClO_4^- source discrimination.

ClO_4^- in the environment is derived from both synthetic and natural sources. Synthetic ClO_4^- salts, including ammonium perchlorate (NH_4ClO_4) and potassium perchlorate ($KClO_4$), have been widely used as oxidants by the military and aerospace industry. A variety of commercial products also contain synthetic ClO_4^-, including fireworks, matches, air bags, chlorine bleach, safety flares, perchloric acid, and chlorate herbicides. Historical disposal practices by the military, aerospace industry, and chemical manufacturers have resulted in groundwater and drinking water contamination with ClO_4^- in the United States. Isolated contamination from fireworks, road flares, explosives, and perchloric acid has also been reported. However, ClO_4^- is also a naturally occurring anion. It is present with sodium nitrate ($NaNO_3$) in surficial deposits in the Atacama Desert of Chile at an average concentration of around 0.1% (by mass) of the total soluble salt, and these deposits (sometimes referred to as "Chilean caliche") were widely used in the United States during the first half of the 20th century as a source of inorganic nitrogen fertilizer. Natural ClO_4^- that is not associated with Chilean fertilizers has also recently been detected in the vadose zone, groundwaters, and mineral deposits collected from the arid southwestern United States, including 155,000 km^2 of groundwater in the Southern High Plains (SHP) of Texas and New Mexico. In addition to synthetic sources, natural ClO_4^- from both Chilean fertilizers and indigenous sources represents a potentially large source of ClO_4^- in groundwater and drinking water in the United States.

1.0 INTRODUCTION

1.1 PERCHLORATE SOURCES

The key objective of the isotopic techniques described herein is to provide evidence concerning the origin of perchlorate (ClO_4^-) in groundwater and, more specifically, whether that ClO_4^- is synthetic or natural. The following sections summarize current information about the sources of synthetic and natural ClO_4^- in the environment and the potential extent of their distribution. Relevant literature is cited to provide sources of additional information about ClO_4^-.

1.1.1 Synthetic Perchlorate

Ammonium perchlorate (NH_4ClO_4) has been used for several decades in the United States as the primary oxidant in a variety of solid rocket propellants and explosives produced for military and aerospace applications. More than 100 varieties of military rocket motors, as well as the solid rocket boosters for the National Aeronautics and Space Administration (NASA) space shuttles, contain NH_4ClO_4 (Cunniff et al., 2006). Potassium perchlorate ($KClO_4$) is also used for many military applications, including U.S. Navy underwater munitions. Besides military propellants and explosives, a variety of commercial products contain synthetic ClO_4^- either intentionally or as a manufacturing by-product, including fireworks, matches, air bags, chlorine bleach (NaOCl), safety flares, perchloric acid, and chlorate herbicides (Aziz and Hatzinger, 2008; Aziz et al., 2006; Trumpolt et al., 2005). Based on U.S. Environmental Protection Agency (USEPA) estimates, approximately 4×10^8 kg (400,000 metric tons) of synthetic ClO_4^- has been produced in the United States since the 1950s, with an average production rate of 7.1×10^6 kg/yr from 1951-1997 (Dasgupta et al., 2006). Historical testing and disposal practices at some military installations, ClO_4^- production facilities, and aerospace sites have resulted in substantial contamination of soils and groundwater at these locations (Figure 1.1 and Appendix B). Many groundwater ClO_4^- plumes, which are often aerially extensive and have concentrations up to several hundred milligrams per liter of ClO_4^-, have been identified and are subject to site assessment and (or) remediation (e.g., Hatzinger, 2005; ITRC, 2008). However, the contribution of other commercial products as non-point or small point sources of synthetic ClO_4^- is much more difficult to assess and quantify, although road flares, blasting agents, and fireworks have been indicated as sources of ClO_4^- in some groundwaters (e.g., Böhlke et al., 2009; MADEP, 2007; Munster and Hanson, 2009). Further information on synthetic ClO_4^- sources can be found in previously published reviews (Trumpolt et al., 2005; ITRC, 2008; Aziz et al., 2006).

1.1.2 Chilean Nitrate Deposits and Fertilizer

Natural ClO_4^- has long been known to co-occur with sodium nitrate ($NaNO_3$) in surficial deposits in the Atacama Desert of Chile at an average concentration of around 0.1 % (by mass) of the total soluble salt, but with concentrations as high as 6.8 % reported (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2005). The nitrate deposits, sometimes referred to as "Chilean caliche," were widely used in the United States during the first half of the 20th century as a source of inorganic nitrogen fertilizer. According to the California Department of Agriculture, more than 477,000 metric tons of Chilean nitrate were used in California as fertilizer between 1923 and 1998 (California Department of Food and Agriculture, 1999). Although man-made nitrogen sources are now used in most fertilizer applications, more than 55,000 metric tons of the Chilean nitrate material was shipped to California between 1995 and 2000, primarily for fertilizer

application. There appears to be significant variability in the final ClO_4^- concentration of processed Chilean nitrate fertilizer (as well as the ore from which it is derived), but values ranging from approximately 1500 to 10,000 mg/kg have been reported in historical samples (Urbansky et al; 2001a, 2001b; Eldridge et al., 2000; Dasgupta et al., 2005). Thus, apart from synthetic sources, past application of Chilean nitrate fertilizer clearly represents a potential source of ClO_4^- in groundwater and drinking water in the United States. Based on a conservative estimate of 2000 mg ClO_4^-/kg Chilean fertilizer (Dasgupta et al., 2005), one metric ton of processed Chilean fertilizer likely contained >2.0 kg of ClO_4^-, enough to contaminate more than 300 million L of groundwater to above the current California maximum contaminant level (MCL) of 6 µg/L. Additional information on Chilean nitrate fertilizers as a source of ClO_4^- can be found in previously published papers (Dasgupta et al., 2005; Ericksen, 1981, 1983; Jackson et al., 2006; Böhlke et al., 2009). It should be noted that some other fertilizer materials, such as kelp, have also been reported to contain ClO_4^-, but the concentrations in these materials, when detected, are generally orders of magnitude lower than those historically present in Chilean nitrate, and they are considered unlikely to be of overall environmental significance (Dasgupta et al., 2005; Böhlke et al., 2009).

1.1.3 Indigenous Natural Perchlorate in the United States

Natural ClO_4^- that is not associated with fertilizers from the Atacama has also recently been detected in soils, groundwaters, and mineral deposits collected from the arid southwestern U.S., including groundwater underlying an area of 155,000 km^2 in the Southern High Plains (SHP) of Texas and New Mexico (Rajagopolan et al., 2006; Jackson et al., 2004, 2005, 2006). Based on groundwater age dating, some New Mexico samples (with ClO_4^- concentrations ranging from ~ 0.12 to 1.8 µg/L) were recharged many thousands of years before present, indicating pre-anthropogenic (natural) ClO_4^- sources and accumulation processes (Plummer et al., 2006). This "indigenous" natural ClO_4^- is hypothesized to form initially in the stratosphere through photochemical reactions (Murphy and Thomson, 2000; Dasgupta et al., 2005; Bao and Gu, 2004; Sturchio et al., 2009) and subsequently to deposit at the Earth's surface via precipitation or dry deposition. This hypothesis was supported by a recent study reporting the existence of natural ClO_4^- in precipitation from National Atmospheric Deposition Program (NADP) collectors at 26 sites across the contiguous United States, Puerto Rico, and Alaska over a 3yr period at concentrations ranging from <5 ng/L to 102 ng/L (amount of substance [n]=1578) (Rajagopalan et al., 2009). In arid regions, such as parts of the southwestern United States, ClO_4^- in rainwater and dry deposition is expected to accumulate with time in the vadose zone, along with other deposited salts. This hypothesis was confirmed by Rao et al. (2007), who detected ClO_4^- in the vadose zone at several sites in the Southwest with an average accumulated mass per unit area of 408±88 g/ha. The ClO_4^- concentrations were correlated (r=0.59-0.99) to meteoric chloride (Cl^-) accumulated over the last 6 to 100 thousand years (kyr), indicating that these anions were deposited together via similar processes. Natural indigenous ClO_4^- has also recently been observed to be associated with natural NO_3^- deposits in Death Valley, CA, at concentrations ranging from 0.25 to 1.7 mg/kg (Jackson et al., 2010).

In undisturbed arid regions, atmospheric ClO_4^- is expected to remain primarily in surficial deposits and soils. However, when such environments become subject to large-scale irrigation, such as in the Southern High Plains and other agricultural regions of the western United States, mobilization of ClO_4^- accumulated in the vadose zone to groundwater is likely. Such agricultural

mobilization is hypothesized to account for the high ClO_4^- concentrations observed in groundwater in West Texas, which has been widely irrigated for several decades for production of cotton and other crops (Rajagopalan et al., 2006). Irrigation is also a likely route of transport to groundwater of ClO_4^- applied to crops with Chilean nitrate fertilizers.

1.1.4 USEPA Guidance on Perchlorate Occurrence

The USEPA has been evaluating the occurrence of ClO_4^- for more than a decade and recognizes that the chemical is both widespread in the United States and has synthetic and natural origins. Figure 1.1 illustrates the location of various ClO_4^- manufactures and known releases in the United States, and Appendix B provides more detailed information concerning ClO_4^- manufacturers and users (Mayer, 2003). Additional information on ClO_4^- from the USEPA is available online (http://water.epa.gov/drink/contaminants/unregulated/perchlorate.cfm) and in a recent "Fact Sheet" issued by the agency (USEPA, 2009).

Figure 1.1. Perchlorate manufacturers and users (top panel) and releases as of April 2003. Maps from Mayer (2003).
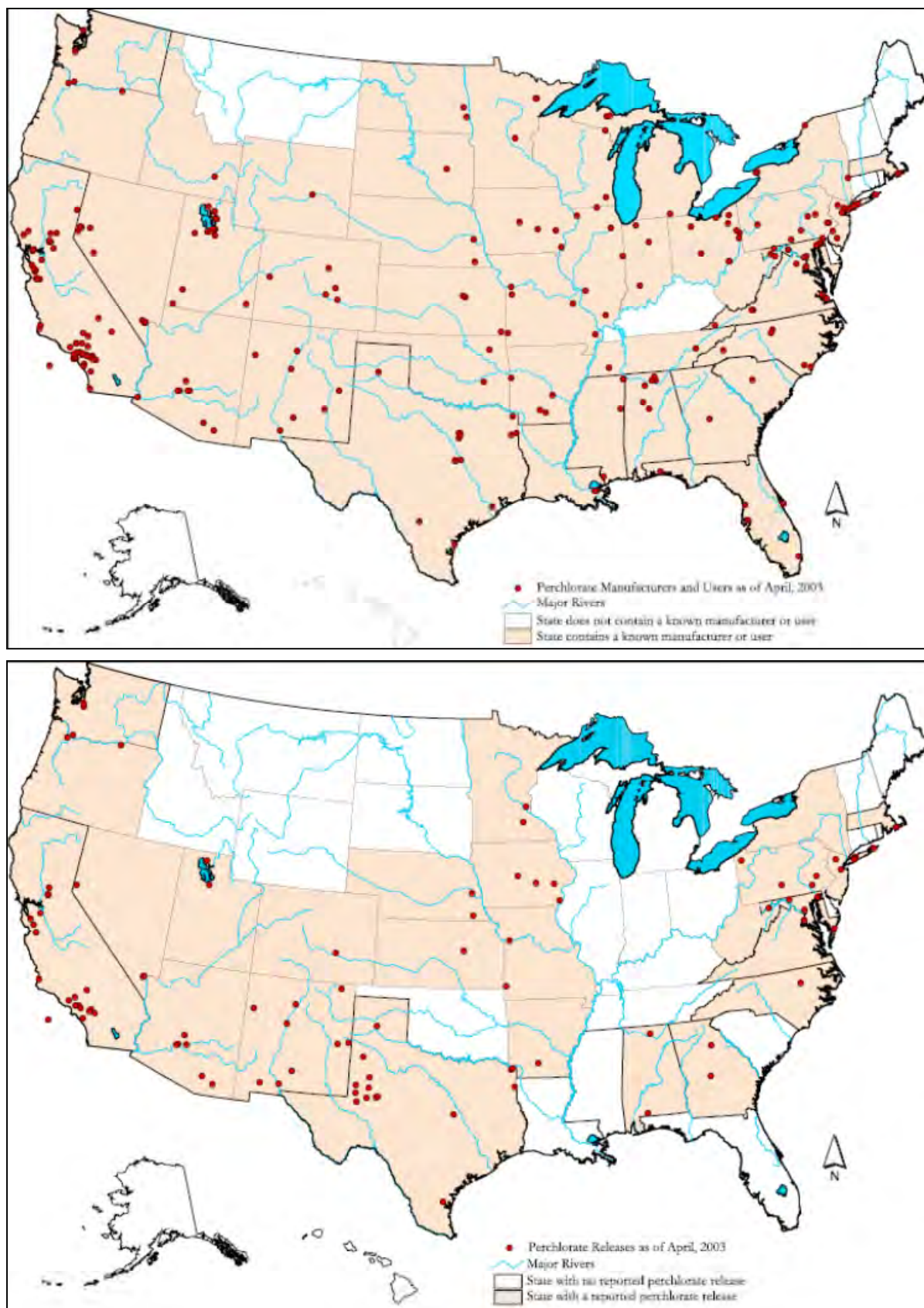
1.2 PERCHLORATE SOURCE IDENTIFICATION

With increasing state and federal regulatory pressure to clean up ClO_4^- in groundwater and drinking water to low part-per-billion (ppb) or microgram per liter ($\mu g/L$) concentrations, source identification is taking on new importance. Where ClO_4^- is present in groundwater at hundreds to thousands of $\mu g/L$, synthetic sources are likely to be the primary source. However, when ClO_4^- concentrations are relatively low (e.g., <20 $\mu g/L$) and a military, commercial or manufacturing source is not readily apparent or is not indicated based on hydrogeological data (e.g., contamination is upgradient of a known military source area), then natural ClO_4^-, either from Chilean fertilizers or natural sources indigenous to the United States, should be considered as a potential source in addition to non-point synthetic sources such as road flares, blasting agents, and fireworks. This is particularly true in historical agricultural areas that may have been subject to both fertilization and irrigation.

The most common analytical method to quantify ClO_4^- concentrations in water and other matrices, USEPA Method 314.0 (ion chromatography) (USEPA, 1999) is incapable of distinguishing natural from synthetic ClO_4^-. Other second-generation methods for ClO_4^- analysis – including USEPA Method 331.0 (ion chromatography with electrospray ionization/mass spectrometry; USEPA, 2005a), USEPA Method 332.0 (high-performance liquid chromatography with electrospray ionization/mass spectrometry); (USEPA, 2005b); – USEPA Method 6850 (high performance liquid chromatography with electrospray ionization/mass spectrometry, USEPA 2007a), and USEPA Method 6860 (ion chromatography with electrospray ionization/mass spectrometry; USEPA, 2007b), although utilizing mass spectrometry for ClO_4^- detection, also cannot measure relative isotopic abundances with the sensitivity and precision required for forensic analysis. A summary of these and other analytical methods for ClO_4^- is provided in USEPA (2009).

The main approach described in this document, chlorine and oxygen isotopic analysis of ClO_4^-, is the primary direct method whereby different sources of ClO_4^- may be distinguished from each other. This approach yields accurate and precise measurements of the relative abundances of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- using isotope-ratio mass-spectrometry (IRMS) as described further in Sections 2.4 and 2.5. It also can yield the relative abundance of the radioactive chlorine isotope ^{36}Cl using accelerator mass spectrometry (AMS), as described further in Section 2.6. Altogether, these measurements provide four independent quantities (isotope abundance ratios) for distinguishing ClO_4^- sources and potential transformations in the environment.

Other isotopic, chemical, and geochemical techniques that can be applied in conjunction with isotopic analyses of ClO_4^- to provide supporting data are described in Section 2.8. Methods used for Cl and O isotopic analyses of ClO_4^- are presented in the subsequent section to provide background on this general approach, and current isotopic data for ClO_4^- are described in Section 3.0. A case study that illustrates the application of IRMS of Cl and O stable isotopes to distinguish sources of ClO_4^- on Long Island, NY, is provided in Section 4.0.

1.3 STABLE ISOTOPIC ANALYSES

Isotopes of a given element have the same number of protons and electrons (thus defining the element), but a different numbers of neutrons, the latter of which provide mass but no charge.

Some isotopes are subject to nuclear decay and are termed radioactive, while others are stable. The methods for isotopic analyses of ClO_4^- described herein refer primarily to the stable isotopes of Cl and O; analysis of ^{36}Cl, a long-lived radioactive isotope of Cl, also is included as another promising forensics tool. Because isotopes of a given element differ in mass, they exhibit slight behavioral differences, such that a variety of physical, chemical, and biological processes can alter the relative abundances of isotopes of elements in a given chemical compound, a process termed "isotopic fractionation." Isotopic fractionation processes, most of which are mass-dependent (equilibrium and kinetic processes that are based upon mass differences), and some of which are non-mass-dependent (processes that do not occur in proportion to mass differences) commonly cause different samples containing a given element or chemical compound to have distinct isotopic compositions. These different isotope ratios can be indicative of the origin of a molecule and thus have forensic science applications; for example, carbon and chlorine isotope ratios of chlorinated solvents produced in different facilities can have different isotopic compositions (Beneteau et al., 1999). In addition, the stable isotope ratios of elements in a parent molecule often change systematically during biodegradation and other degradation processes (e.g., Hunkeler et al., 2008); thus, stable isotope methods can provide unique insights into *in situ* transformation processes and natural attenuation of many constituents in the environment. Additional details and reviews of stable isotope terminology and general principles are provided elsewhere (Hunkeler et al., 2008; Sharp, 2007; Clark and Fritz, 1997; Kendall and Caldwell, 1998; Coplen, 1994).

As noted previously, measurements of stable isotopic composition are conducted using an IRMS. This instrument is designed to measure precisely the relative differences in the isotope ratios of a given element between different substances, rather than the actual absolute ratios in any given substance, which are more difficult to determine accurately. Relative stable isotope ratios of elements are generally reported as differences from those of internationally recognized measurement standards so that measurements from different laboratories can be compared. The relative differences of isotope ratios are reported as "delta" (δ or Δ) values (Coplen, 1994). The general expression used to report relative abundances of stable isotopes is provided below in Equation 2.1, with Cl isotopes (^{37}Cl and ^{35}Cl) as an example.

[Eq. 2.1] $\delta^{37}Cl_{P/Q} = [R(^{37}Cl/^{35}Cl)_P - R(^{37}Cl/^{35}Cl)_Q] / R(^{37}Cl/^{35}Cl)_Q$

Where R=ratio of the atomic or molar abundances (N, number of entities; alternatively n, amount of substance) of two isotopes of an element, with the isotope of higher atomic mass normally in the numerator, in this case: $R(^{37}Cl/^{35}Cl) = N(^{37}Cl)/N(^{35}Cl) = n(^{37}Cl)/n(^{35}Cl)$

$R(^{37}Cl/^{35}Cl)_P$=number ratio of isotopes in substance P

$R(^{37}Cl/^{35}Cl)_Q$=number ratio of isotopes in substance Q

The international measurement standard for $\delta^{37}Cl$ is Standard Mean Ocean Chloride (SMOC), which takes the place of substance Q in Equation 2.1 for reporting the $\delta^{37}Cl$ value of a sample (substance P in Equation 2.1), unless stated otherwise. Because delta values (e.g., $\delta^{37}Cl$) typically are small, they commonly are reported in parts per thousand (per mil, with symbol ‰). A positive δ value indicates that the ratio of the heavy/light isotopes in the sample is higher than

that of the standard, while a negative δ value indicates that the ratio of the heavy/light isotopes in the sample is lower than that of the standard. For example, if $\delta^{37}Cl$ is reported as -18‰, this means that $R(^{37}Cl/^{35}Cl)$ in the sample is 18 parts-per-thousand or 1.8% lower than $R(^{37}Cl/^{35}Cl)$ in the standard (SMOC), for which the $\delta^{37}Cl$ value would be 0 by definition. It is important to note that absolute isotope ratios (R) are difficult to measure as precisely as relative differences of isotope ratios (δ), so that most IRMS equipment and techniques are designed to produce high-precision comparisons of the isotope ratios of samples and standards. The value of $R(^{37}Cl/^{35}Cl)$ in seawater has been reported as 0.31940 ± 0.00007 (Xiao et al., 2002) and found to be homogeneous (to within ±0.1 ‰) in samples of seawater from around the world (Godon et al., 2004). In practice, stable isotope laboratories typically have quantities of secondary isotope reference materials that are used routinely. These secondary reference materials are calibrated against internationally recognized reference materials such as those provided by the National Institute of Standards and Technology (NIST) or the International Atomic Energy Agency (IAEA). The secondary isotope reference materials must be isotopically homogeneous at the scale of analysis. In addition, it is preferred that isotopic reference materials be similar chemically to the samples being analyzed and that samples and reference materials are analyzed together using identical procedures, as discussed in Sections 2.4 and 2.5 (see also Werner and Brand, 2001). For oxygen stable isotopes, the international measurement standard is Vienna Standard Mean Ocean Water (VSMOW), for which $\delta^{17}O$ and $\delta^{18}O$ are exactly 0 by definition.

1.4 ISOTOPES OF CHLORINE AND OXYGEN IN PERCHLORATE

Both of the elements comprising the ClO_4^- molecule (i.e., Cl and O) have more than one stable isotope. Oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O), which have molar abundances (mole fractions) of approximately 99.76206%, 0.03790%, and 0.20004%, respectively, in the VSMOW standard (Coplen et al., 2002). Chlorine has two stable isotopes (^{35}Cl and ^{37}Cl), with molar abundances of approximately 75.779% and 24.221%, respectively, in the SMOC standard (Coplen et al., 2002). Chlorine also has a long-lived radioactive isotope (^{36}Cl) with a half-life of ~301,000 yr, whose relative abundance is small (typically $<10^{-15}$ to 10^{-12} relative to the stable Cl isotopes) but can be useful for studying origins of Cl-bearing compounds (Phillips, 2000). Techniques to determine relative stable isotope ratios of chlorine (^{37}Cl and ^{35}Cl) in the ClO_4^- molecule were first reported by Ader et al. (2001) and Sturchio et al. (2003). Subsequently, methods for analysis of relative isotope ratios of oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- were described (Bao and Gu, 2004; Böhlke et al., 2005). Methods to collect and purify ClO_4^- from environmental samples, including groundwater, minerals, and soils have been progressing for several years, as have the relevant IRMS techniques for Cl and O isotopic analyses of ClO_4^-. Recent developments in these methods are summarized in several different papers and book chapters (Gu et al., 2011; Sturchio et al., 2007, 2011; Jackson et al., 2010; Böhlke et al., 2009; Hatzinger et al., 2009). The first analyses of ^{36}Cl in different ClO_4^- samples also was reported recently (Sturchio et al., 2009). The results gained from analyses of O and Cl stable isotopes and ^{36}Cl in ClO_4^- using these new methods provide critical insight into the origins of ClO_4^-, both as an environmental contaminant and a naturally formed anion in the environment. These results are described in Section 3.0.

One objective of this guidance manual is to provide details concerning the methodology used to (1) collect ClO_4^- samples from the environment, particularly from groundwater, which is the main medium of interest for ClO_4^- source identification; (2) purify the collected ClO_4^- samples;

(3) conduct O and Cl isotopic analyses on the purified samples; and (4) determine probable sources using the resulting isotope data. These details are provided in Section 2.0 (sample collection, purification, and isotopic analyses) and Section 3.0 (current isotope data and evaluation of sources). In addition, some types of supporting information that are often useful for evaluating ClO_4^- isotopic data are provided in Section 2.8, and a case study of source evaluation in groundwater on Long Island is given in Section 4.0. It should be noted that, compared to many other environmental sampling and analysis techniques, compound-specific stable isotopic analysis (CSIA) is a relatively specialized technique that continues to evolve, and ClO_4^- stable isotopic analyses have only been performed since 2004. Thus, the techniques and quality assurance/quality control (QA/QC) parameters are still being refined, and there are no USEPA-certified methods for CSIA of organic or inorganic compounds. However, a recent document from the USEPA, which acknowledges both the utility of CSIA as well as the newness of this approach, provides "...general recommendations on good practice for sampling groundwater for CSIA, and quality assurance recommendations for measurement of isotope ratios." (Hunkeler et al., 2008). While the USEPA document is focused primarily on (1) carbon isotopic analysis in organic compounds and (2) utilizing CSIA to document biodegradation, some of the general principles apply to Cl and O isotopic analyses of ClO_4^- and are cited herein where appropriate.

This guidance document primarily describes the sampling and analysis methods that have been developed and are now used routinely for measuring Cl and O isotope ratios in ClO_4^-, and it provides initial recommendations for appropriate QA/QC protocols. This document, along with the growing published, peer-reviewed literature on Cl and O isotopic analyses of ClO_4^-, is intended to provide guidance concerning the application of the method and a summary of the data generated by the method to date.

2.0 METHODS OF SAMPLING AND ANALYSIS

2.1 BASIC PROCEDURES

This section of the document is designed to provide guidance for the sampling and analysis of ClO_4^- for Cl and O stable isotopes and ^{36}Cl in water samples, including recommendations for QA/QC. Some details are also provided for sample collection and processing from solid media, such as soils. Methods for determining the isotopic composition of ClO_4^- consist of six basic steps:

    (1) Sampling using ion exchange (IX) columns
    (2) Extraction and purification of ClO_4^- from IX columns
    (3) Verification of sample purity
    (4) Analysis of stable O isotopes in ClO_4^- by IRMS
    (5) Analysis of stable Cl isotopes in ClO_4^- by IRMS
    (6) Analysis of ^{36}Cl by AMS.

Abbreviated descriptions of the fundamental methods utilized for this procedure have been published in several peer-reviewed papers and book chapters, including Bao and Gu (2004); Sturchio et al. (2006, 2007, 2009, 2011); Böhlke et al. (2005, 2009); Hatzinger et al. (2009); Jackson et al. (2010); and Gu et al. (2011). Because these methods are still evolving as part of ongoing SERDP (ER-1435) and ESTCP (ER-200509) projects, various procedures described herein are likely to undergo modification and refinement with time. However, the method described herein and in the aforementioned literature has thus far proven to be a robust approach to evaluate ClO_4^- sources in groundwater and represents the current state-of-the art at the time of preparation of this document.

2.2 SAMPLING USING ION EXCHANGE (IX) COLUMNS

Approximately 20 mircomoles (µmol) of pure ClO_4^- salt (as $CsClO_4$ or KClO4, prepared as described in Section 2.3), is normally sufficient to obtain duplicate stable isotope ratio measurements by IRMS for both O and Cl in the ClO_4^- ion. However, because of potential losses during sample purification (Section 2.3), and allowing sufficient sample for ^{36}Cl and replicate analyses, it is desirable to collect samples containing at least 100 µmol (i.e., 10 mg) of ClO_4^- from each source. The following sections focus on sample collection from a groundwater source, which is the most typical application of this method. Section 2.2.8 provides a brief description of sampling techniques for soils. For groundwaters with low ClO_4^- concentrations (i.e., <10 µg/L), collecting 10 mg of ClO_4^- can be challenging. For example, if the ClO_4^- concentration in a well is 5 µg/L, then 2000 L (~530 gal) of water is required to obtain the necessary 10 mg. Shipping this volume of water is impractical. Rather, small columns containing about 100 mL (~60 g dry wt) of Purolite A-530E ClO_4^--specific anion exchange resin (IX resin) have been developed and deployed routinely for field use. Water is passed through these columns, and the ClO_4^- is trapped by the IX resin. Although many hours may be required for sample collection in some cases (flow rates up to 2 L/min are recommended), the columns are capable of trapping 10 mg of ClO_4^- on a small volume of resin. Water bodies with ClO_4^- concentrations as low as 0.05 µg/L have been sampled successfully with cumulative pumping times of days to weeks. The

ClO_4^- is then extracted from the resin and purified prior to IRMS analyses, as described in Section 2.3.

2.2.1 Sampling Column Construction

The sampling columns used to collect ClO_4^- in the field are custom made. They are simple to construct, and various design modifications are possible based on the specific application. The design and materials for a typical 100 mL sampling column are provided in Figure 2.1. This basic column design has been used in the field for ClO_4^- sample collection at numerous sites (e.g., Böhlke et al., 2005, 2009; Jackson et al., 2010). The column consists of a 1-1/4-inch Schedule 80 polyvinyl chloride (PVC) pipe (Figure, 2.1, Item D). Clear PVC is recommended so that the resin is visible during sampling, and any channeling of groundwater or trapped air can be observed and corrected. To construct the column, a Teflon or stainless steel screen (100 mesh) is initially cut in a circle to a diameter of 1-5/8 inches, which matches the outer diameter (OD) of the clear PVC pipe. The screen is then glued in place on one end of the pipe. A 1-1/4-inch Schedule 40 PVC end cap (Figure 2.1, Item E) is then packed partially with glass wool or glass fiber filters (to fill the void in the end cap between the screen and the end of the cap) and glued with PVC primer and glue to the column body. The end cap should be drilled in the center (1/4 inch bit) and fitted with a 1/4 x 1/8-inch National Pipe Thread (NPT) polypropylene barbed hose fitting (Item A) prior to column construction. A similar-sized brass fitting may be substituted. A 1/4-inch PVC Schedule 40 male adaptor (socket weld with threaded end) should then be glued with PVC glue to the open end of the clear PVC pipe (Figure 2.1, Item G).

At this point in construction, the column can be filled with Purolite A-530E strong base IX resin (Purolite Co., Bala Cynwyd, PA), a bifunctional resin that was originally developed at Oak Ridge National Laboratory, Oak Ridge (ORNL), Tennessee, for selective adsorption of pertechnetate (TcO_4^-) and was found to be equally effective for ClO_4^- (Gu et al., 2000, 2007; Gu and Brown, 2006). Other resins should not be substituted at present because the ClO_4^- extraction process is specific to this resin. The resin should be wet with ClO_4^--free deionized water for a few hours prior to packing to allow expansion, and ~100 mL of wet resin will fill the column to the top of the male adaptor (Figure 2.1, Item G). The column should be gently tapped to remove any air bubbles. Once the resin is added, the top of the column should be covered with a second Teflon or stainless steel screen (1-5/8 inches in diameter). This screen should not be glued. The open end of the column can then be sealed with a threaded 1-1/4-inch Schedule 80 PVC end cap (Figure 2.1, Item F), which is packed partially with glass wool or glass filter fibers and fitted with a 1/4 x 1/8-inch polypropylene or brass barbed hose fitting as described previously for the influent end of the column (Figure 2.1, Item A). The end cap should be threaded tightly. The assembled column should be flushed briefly with deionized water at a flow rate of 2 to 3 L/min to check for potential leaks under simulated field sampling conditions. A single piece of Tygon tubing (1/4-inch inner diameter [ID] by 3/8 inch OD; Fig 2.1, Item B) should then be connected to each of the barb fittings using hose clamps for column storage. It is recommended that the sampling columns are stored at 4° C to prevent any bacterial or fungal growth in the tubing prior to use.

2.2.2 Collection of Perchlorate Samples from Groundwater

A groundwater well can be sampled for ClO_4^- using either a submersible pump (e.g., Grundfos "Redi-flo" or equivalent) or by sampling a sidestream from a municipal supply well or a

household well that already has a submersible or external pump in place. Bladder pumps, bailers, and inertia pumps are generally not suitable for ClO_4^- sampling with IX columns because the pressures and volumes are not usually adequate for sample collection. In those instances in which ClO_4^- concentrations in groundwater are relatively high such that bulk water samples can be collected and transported to the laboratory (e.g., a 5L volume of water from a well with ClO_4^- concentration of 2 mg/L), the aforementioned pumps can be used for groundwater sampling. Typically, however, groundwater with ClO_4^- of unknown origin has concentrations that are far below that necessary to collect bulk water samples.

General procedures for groundwater sampling with a submersible pump are provided in several documents (e.g., Nielsen and Nielsen, 2007; Barcelona et al., 1985), but it should be noted that the details vary by organization (e.g., USGS, USEPA, state environmental agencies), and often by project site. USEPA recommendations for groundwater sampling are provided in Puls and Barcelona (1996) and Yeskis and Zavala (2002) and are summarized for CSIA of organic compounds in Hunkeler et al. (2008). It is recommended that typical procedures for well preparation and purging, which also vary among state and federal regulatory organizations, and sometimes by site, are followed prior to sampling. In general, well purging or preparation either entails (1) calculating the total well casing volume based on well diameter and water depth and pumping two to three well volumes at a rapid rate prior to sampling or (2) pumping water at a continuous flow rate and continuously measuring key field parameters such as pH, oxidation-reduction potential (ORP), turbidity, and dissolved oxygen (DO) with a field meter until they are stable, at which time water samples are collected (Hunkeler et al., 2008; Puls and Barcelona, 1996). Either of these techniques can be used to effectively purge a well prior to collection of ClO_4^- samples for isotopic analysis. However, the flow rates employed using the second approach, which is sometimes called "low-flow" sampling, may need to be increased somewhat compared to typical guidance (i.e., to 2 L/min in some instances). However, as long as field parameters are stable prior to sampling, the groundwater passed through the column should be representative of that entering the screened interval of the well.

During sampling, water is pumped directly from a well or, in some instances from a tap or faucet to the inlet port of the column using tubing, metal, or plastic fittings and connections. Because ClO_4^- has a low affinity for most tubing materials, the tubing selected for sampling is not critical. For submersible pump applications, 1/4-inch ID by 3/8-inch OD polyethylene tubing commonly is used. Because well water commonly has some turbidity due to suspended sediments or other precipitates, it is recommended that a cartridge pre-filter be placed in-line before the IX column to prevent fouling of the IX resin and a consequent increase in pressure across the column. For water with low turbidity, a 5.0-μM high capacity cartridge filter can be used as a pre-filter (e.g., Pall Co., http://labfilters.pall.com/catalog/laboratory_20031.asp). If the water has high turbidity, a large capacity household sediment filter can be placed in-line (e.g., General Electric Co., FXHSC whole house filter). Hose clamps should be used to attach tubing to the IX column, in-line filter, and any other places where the tubing is not continuous (e.g., reducer, etc) and where pressure buildup may occur. A typical column setup for a groundwater well is provided in Figure 2.3. For household sampling, a barbed hose fitting and tubing can be used to connect directly between an outside house faucet and the IX column using polyethylene, Tygon, or other tubing. A cartridge pre-filter generally is not required for this application.

Columns should be operated in an upflow direction (vertical orientation) and the flow direction should be marked. For the typical 100mL column setup, as shown in Figures 2.1-2.3, it is recommended that flow rates not exceed 2 L/min to allow adequate residence time for ClO_4^- adsorption in the IX resin within the column. Prior to initiating groundwater flow through the column, and periodically thereafter (with intervals determined by expected sampling time), groundwater samples may be collected prior to the IX column (influent) and after the column (effluent) for analysis of ClO_4^- concentration by USEPA Method 314.0 or other certified method. In instances where influent concentrations of ClO_4^- to the columns are low (e.g., <2 μg/L), more sensitive mass-spectrometric methods may be required for these analyses (see Section 1.2). For U.S. Department of Defense (DoD) applications, sample collection procedures and certified methods are available (DoD, 2007). If the sampling is expected to take several hours based on the groundwater concentration, which is typical, hourly sampling of influent and effluent is recommended. The flow rate of water through the column should also be recorded when the samples are collected and adjusted, if necessary. For shorter sampling events, more frequent influent and effluent samples can be taken (e.g., every 1/2 hr for a 3hr sample collection). The concentration measurements and flow rates during each sampling event allow a mass balance determination to be conducted for ClO_4^- (i.e., how much ClO_4^- is expected on each IX column). Groundwater should be passed through each column until an estimated mass of 10 mg of ClO_4^- is present on the resin, based on influent concentrations and flow rate. For example, if the influent ClO_4^- concentration is 3 μg/L and the flow rate to the column is 2 L/min, then 360 μg of ClO_4^- is expected to be adsorbed in the resin for each hour of operation. Thus, a total collection time of 28 hr would be recommended for collection of the desired 10 mg of ClO_4^-.

Breakthrough of ClO_4^- from IX columns can occur in groundwater, particularly in groundwater with high nitrate/perchlorate (NO_3^-/ClO_4^-) ratios or elevated dissolved organic carbon (DOC) concentrations. In most groundwaters, breakthrough of ClO_4^- will be <10% of the total ClO_4^- concentration in the influent water. However, in instances in which influent NO_3^- concentrations are high (e.g., >1 mM NO_3^-), higher ClO_4^- breakthrough can occur with time. As part of ESTCP Project ER-200509, experiments have been conducted to determine whether isotopic fractionation of O or Cl in ClO_4^- occurs as a function of the fraction of ClO_4^- breakthrough. These results are not yet published. However, preliminary data indicate that the change in O isotope values is negligible for $\Delta^{17}O$ even if the concentration of ClO_4^- in the column effluent reaches >90% of the influent concentration (i.e., <10% retention on the column, which is far greater breakthrough than expected or previously observed in a field setting). Slight, but measurable, isotopic fractionation was indicated by $\delta^{18}O$ data when there was an artificially high fraction of ClO_4^- breakthrough. The change in $\delta^{18}O$ in samples with >90% breakthrough in effluent compared to influent (which occurred in laboratory columns receiving 2 μM ClO_4^- and 160 mM nitrate as nitrogen [NO_3-N]) was ~1‰, which, while statistically significant, is not large enough to alter conclusions in forensic evaluations based on the current measured values of synthetic ClO_4^-, Chilean nitrate-associated ClO_4^-, or indigenous natural ClO_4^- (See Section 3.0). Preliminary data indicate corresponding changes in $\delta^{37}Cl$ accompanying column breakthrough are smaller than those of $\delta^{18}O$.

2.2.3 Sample Replication and Split Samples
In many instances, single IX columns are collected from each well. However, it is possible to collect replicate samples from a single well during sampling by connecting multiple IX columns

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to a single submersible pump, as shown in Figure 2.3. Most submersible pumps will easily supply the flow needed for duplicate columns if the well yield is adequate. One difficulty with this approach is that flow through the columns may vary with time if different backpressures develop. This may be resolved by connecting an adjustable valve in place to split the flow rather than a simple Y splitter in the tubing, as represented in Figure 2.3, and adjusting relative flow to each column with time. If sufficient ClO_4^- is trapped on each column, duplicate samples will be available for extraction and isotopic analysis, thus allowing evaluation of method precision. It is also possible to preserve (with 0.05 N hydrochloric acid [HCl] as described in Section 2.2.4) and archive the duplicate column for analysis in the event that the first sample is lost or otherwise compromised during analysis. When wells have very low ClO_4^- concentrations (e.g., <1 µg/L), duplicate columns are recommended (if feasible, based on well yield) to increase the total ClO_4^- collected with time. In this case, the contents of the columns can be combined to a single sample during processing to ensure that enough ClO_4^- is available for analysis.

Split samples are often collected from one or more wells during a field project to compare results between analytical laboratories and verify results from the contracted laboratory (e.g., Nielsen and Nielsen, 2007; Keefe et al., 2003). These samples are either collected close together in time or they are prepared by homogenizing a single sample, and then the replicates are shipped to two different laboratories. Although similar practices would be desirable for determination of Cl and O isotopic composition of ClO_4^-, there is only one laboratory currently that conducts sample preparation and analysis as a commercial service (See Section 5.0); thus, a true sample split currently is not possible. If other commercial laboratories offer these services in the future, split sampling will be possible.
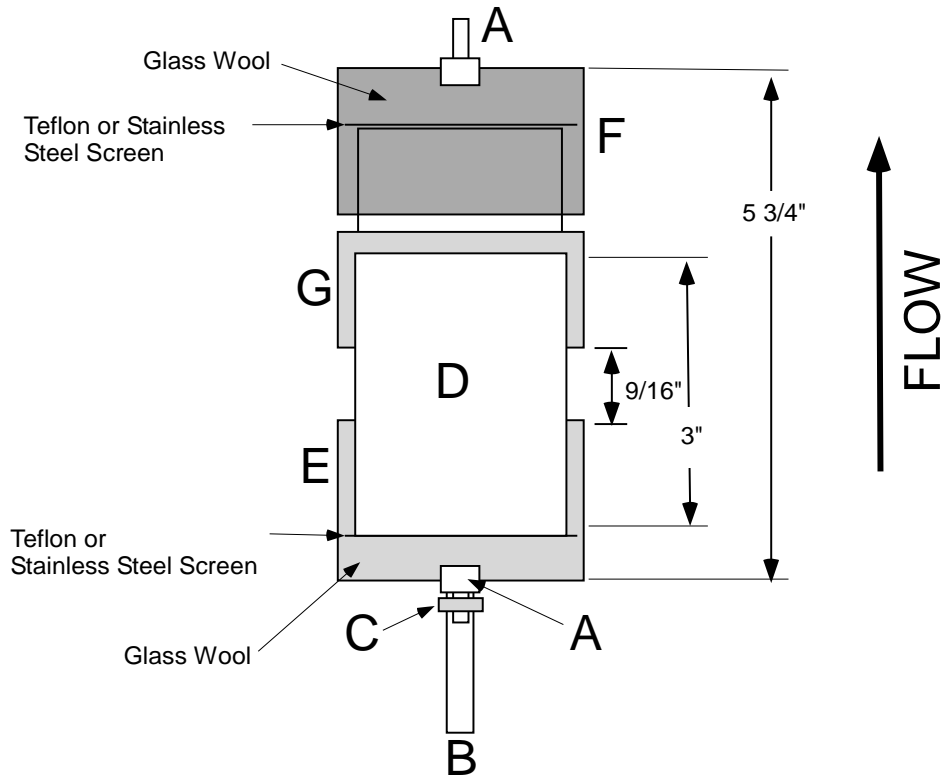
Figure 2.1. Schematic diagram of ion exchange (IX) column used to collect ClO_4^- from groundwater.

Figure 2.2. Photograph of (A) IX column used to collect ClO_4^- from groundwater and (B) column attached to well during sample collection.
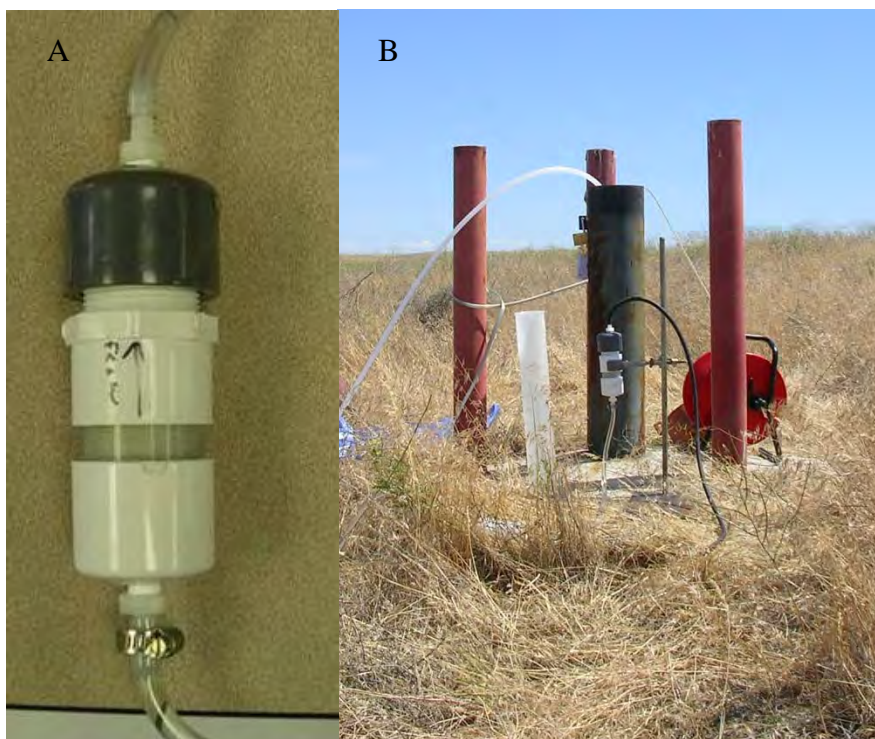
Figure 2.3. Typical setup of ClO$_4^-$ sampling equipment at a groundwater well. A duplicate column is recommended but optional.
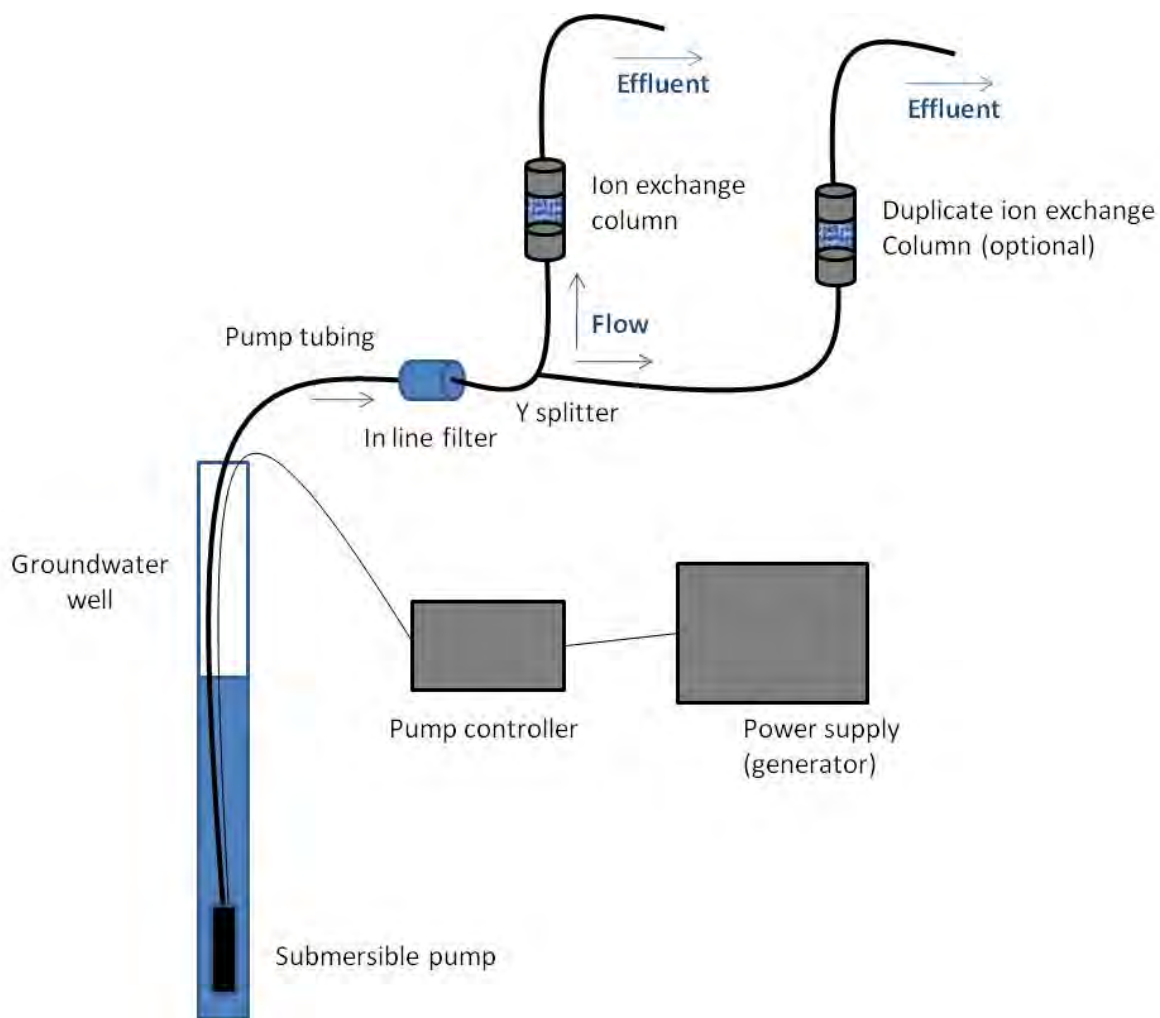
2.2.4 Sample Preservation and Shipment
Once the desired amount of water has been passed through the IX column to collect ClO_4, the column should be disconnected from the pump, drained of standing water, and sealed by attaching a small piece of tubing from one end to the other (i.e., attached to the hose barbs on each end with a hose clamp). Alternatively, hose barbs may be removed and replaced with threaded plugs. The resin should remain moist but not saturated with water. The column should then be placed in double Ziploc-style storage bags and stored or shipped at 4° C for preservation prior to processing. In most instances, ClO_4^- will be stable on the column under these conditions because air is present in the column, and ClO_4^- biodegradation does not occur under aerobic conditions (Coates and Achenbach, 2004). Adsorption of the ClO_4^- onto the resin is also expected to inhibit biodegradation. However, if a sample is collected from anoxic groundwater or water with high total organic carbon content (e.g., lake water, groundwater amended with a substrate to enhance biodegradation, etc), the potential for ClO_4^- biodegradation on the column exists. In these instances, dilute HCl can be used to preserve the column prior to processing. To preserve with HCl, the column should be drained of groundwater, and then the resin should be saturated with a solution of 0.05 N HCl, which will reduce the pH to <2 (Hatzinger et al., 2009). The ends should then be sealed with a single piece of tubing using hose clamps as described previously, and the column should be placed in double Ziploc-style storage bags. The preserved columns should be stored or shipped at 4° C prior to processing. At present, columns do not have a maximum hold time prior to extraction and analysis.

2.2.5 Column Identification and Chain-of-Custody
Basic chain-of-custody (COC) procedures used for typical groundwater sampling should also be used for ClO_4^- sampling. These procedures vary somewhat by state or regulatory organization, and sometimes by site. Appropriate procedures should be reviewed and followed. Prior to groundwater sample collection, each IX column should initially be labeled with a unique identifier (tags or permanent ink marking), as well as the sample well location and ID. This column ID number should also be recorded on a COC form prepared during the sampling event along with the well identification number and location. During groundwater pumping, a record should be kept of the start and end time of groundwater pumping, the flow rate (measured multiple times during the pumping period), and the time of influent and effluent sampling. The influent and effluent samples should be recorded on the COC form by time as is standard procedure for most groundwater samples collected for routine analyses.

2.2.6 Relevant Blanks for Perchlorate Sampling
When volatile organic compounds (VOCs) or other contaminants are sampled by grab methods, a series of different blanks are often collected, including field blanks, equipment blanks, filter blanks, and trip blanks (e.g., see Keefe et al., 2003). Most of these blanks are designed to determine if sampling procedures or equipment have caused cross-contamination of samples or if background contamination exists in sample bottles or preservatives. Because of the unique nature of sampling ClO_4^- for isotopic analyses, which employs IX columns (rather than sample bottles) to collect milligram quantities of ClO_4^- from hundreds to thousands of liters of water, trace contamination with ClO_4^- is unlikely to affect results. This is in contrast to many other methods, such as VOC sampling, where contamination of a sample or bottle with 1 µg/L of a chemical is often important and needs to be identified. Moreover, many of the types of blanks used for typical grab sampling for concentration are not easily transferred to the IX method used

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for isotope samples. For this reason, blank samples typical of VOC or other sampling are not generally used or deemed necessary in ClO_4^- sampling for isotopic analyses.

However, based on current methods, the following guidance is provided on the potential application of blank samples for field projects involving sample collection for Cl and O isotopic analyses of ClO_4^-:

1. Field Blank. Field blanks are often used to determine if contamination exists in sample bottles or bottle preservatives. The blanks are filled with certified contaminant-free water in the field and analyzed in the analytical laboratory for contamination. This approach is applicable and recommended in instances where ClO_4^- concentrations of the order of milligrams per liter are present in groundwater and samples are shipped to the laboratory in bottles rather than adsorbed in IX columns. For reasons noted above, it is difficult to determine how to prepare an appropriate field blank when IX column sampling is conducted because hundreds to thousands of liters of water are passed through the column in the field. It is not practical to simulate this process in the field using ClO_4^--free water due to the volumes required. Thus, this type of blank is not currently deemed necessary. An equipment blank (see below) can be used to ensure that the columns or resin do not contain ClO_4^- prior to sample collection.

2. Equipment/Rinse Blank (Analytical Procedure Blank). An IX column equipment blank can be prepared to ensure that the IX resin or column sampling device is not contaminated with ClO_4^-. To prepare this blank, one column that is manufactured along with those used to collect ClO_4^- from groundwater at a site should be preserved and processed with the other sample columns. No groundwater should be passed through this column prior to processing. ClO_4^- should not be present above trace level in the extract from this column (<10 µg total recovered). In addition to this approach, ClO_4^- can be measured in each lot of Purolite A530E resin that is used to prepare sampling columns to ensure that the resin is free of ClO_4^-. Because this resin is certified for use in drinking water treatment systems for ClO_4^-, and it is not recycled, contamination of virgin resin with ClO_4^- is unlikely.

    In addition, good management practices should be used when transferring a submersible pump between wells, including thoroughly decontaminating the pump with clean (ClO_4^--free) water and either thoroughly washing or replacing the tubing. However, because ClO_4^- does not adsorb in most tubing material and is completely soluble, the risk of significant contamination of an isotope sample due to carry-over between wells is minimal. Thus, equipment blanks from pumps can be taken to ensure good management practices are followed, but they are not critical for ClO_4^- sampling for isotopic analyses.

3. Trip Blank. A trip blank is generally prepared in the laboratory using analyte-free water, shipped with the sample containers to the field, and then returned to the laboratory unopened to assess sample contamination during transport. For isotopic analyses, the approach previously described for an IX column equipment blank should also be sufficient as a trip blank, if the column is transported with all other sampling columns to the field but not used in sampling activities. As previously noted, the potential for an IX sampling column to

become inadvertently contaminated with a quantity of ClO_4^- large enough to affect isotope results during shipping or routine well sampling is considered highly unlikely.

2.2.7 Summary of QA/QC Procedures for Groundwater Sampling
The following is a summary list of basic QA/QC procedures used to sample ClO_4^- for O and Cl isotopic analyses that have been covered in the previous section.

1. Each IX column should be individually tagged or marked with permanent ink, and the column identifier should be recorded in a field book and a COC form for each well sampled.

2. Duplicate columns should be collected for an individual groundwater well when possible.

3. A meaningful field blank is not practical when using an IX column for sampling but can be prepared in instances where water samples (rather than IX columns) are shipped. An equipment blank can be prepared by extracting and analyzing ClO_4^- from an IX column that has not been used in the field for sampling.

4. Each groundwater well should be purged according to accepted procedures for an individual site as outlined in Section 2.2.2 prior to sampling.

5. The column should be operated in an upright position at ≤ 2 L/min and the flow rate should be recorded and adjusted periodically during the collection time. Influent and effluent samples should be collected from each column periodically for subsequent analysis of ClO_4^- concentration.

6. Once sampling is complete, columns should be drained, and the ends sealed with a single piece of tubing. The sealed column should then be sealed in a Ziploc-style bag and placed at 4° C. Shipping to the analytical laboratory should be done on ice prior to ClO_4^- extraction and analysis.

7. Additional column preservation by saturating the resin with 0.05 molar (M) HCl is recommended if ClO_4^- is collected from an anoxic aquifer or location where biodegradation is likely or if extended storage is expected (e.g., archived sample). The column should be sealed in a Ziploc-style bag and placed at 4° C after preservation with HCl.

2.2.8 Soil Sampling Procedures
Perchlorate for isotopic analysis can be extracted from solid samples of surficial salt deposits, surface soils, and the deep vadose zone. The basic procedure for collection was described recently by Jackson et al. (2010). Initially, the concentration of ClO_4^- in the bulk material should be determined by collecting several solid samples, extracting soluble salts from the samples with ClO_4^--free water, and then measuring the ClO_4^- concentration by an accepted analytical method for soils (e.g., USEPA, 2007). The total amount of solid material that must be extracted (leached) to collect the required milligram quantities of ClO_4^- for purification and isotopic analysis can then be determined. Because ClO_4^- is highly soluble in water, it can be removed readily from dispersed solids by aqueous leaching. Vadose-zone material containing ClO_4^- can be collected using a backhoe, placed on a tarp or other clean surface to isolate it from surrounding soils, and

extracted with ClO_4^--free water (Jackson et al., 2010). It is important to remove any ClO_4^- from the water source used for solid extraction, which can be accomplished by initially passing that water through a large column of Purolite A530E resin prior to use, as described in Jackson et al. (2010).

Extraction of ClO_4^- from solids can be conducted in small batches by adding solid material (40 to 60 kg) and water (~80 L) in a clean cement mixer, mixing the slurry for ~10 min, then decanting the liquid into a large polyethylene drum or other container (Figure 2.4). After sediments settle in the drums, the overlying water (with dissolved ClO_4^-) is pumped to a clean container, then passed through a sediment pre-filter (e.g., 50-µM pore-size; General Electric Co., Trevose, PA) and an IX resin column in sequence, as described previously for groundwater sampling (see Figures 2.3 and 2.4). Influent and effluent samples should be collected periodically to determine the concentration of ClO_4^- in water applied to the column and the efficiency of ClO_4^- removal as described for groundwater in Section 2.2.2.   After the extraction process, basic QA/QC procedures described for groundwater sampling are applicable. In addition to these procedures, it is advisable to wash any equipment used for soil mixing and to determine that the vessels are free from outside contamination with ClO_4^- by analyzing rinse water. It should be noted that for ClO_4^- at low microgram-per-kilogram concentrations in solid material, extraction of several thousand kilograms of solids may be required to obtain sufficient ClO_4^- for Cl and O isotopic analyses.

Figure 2.4. Extraction of ClO_4^- from vadose-zone sediment in West Texas.   (A) Collection of ClO_4^- from decanted soil extracts on IX columns after passing through a sediment filter. (B) Extraction of ClO_4^- from soil by slurrying in cement mixers. (see Jackson et al., 2010 for further details).
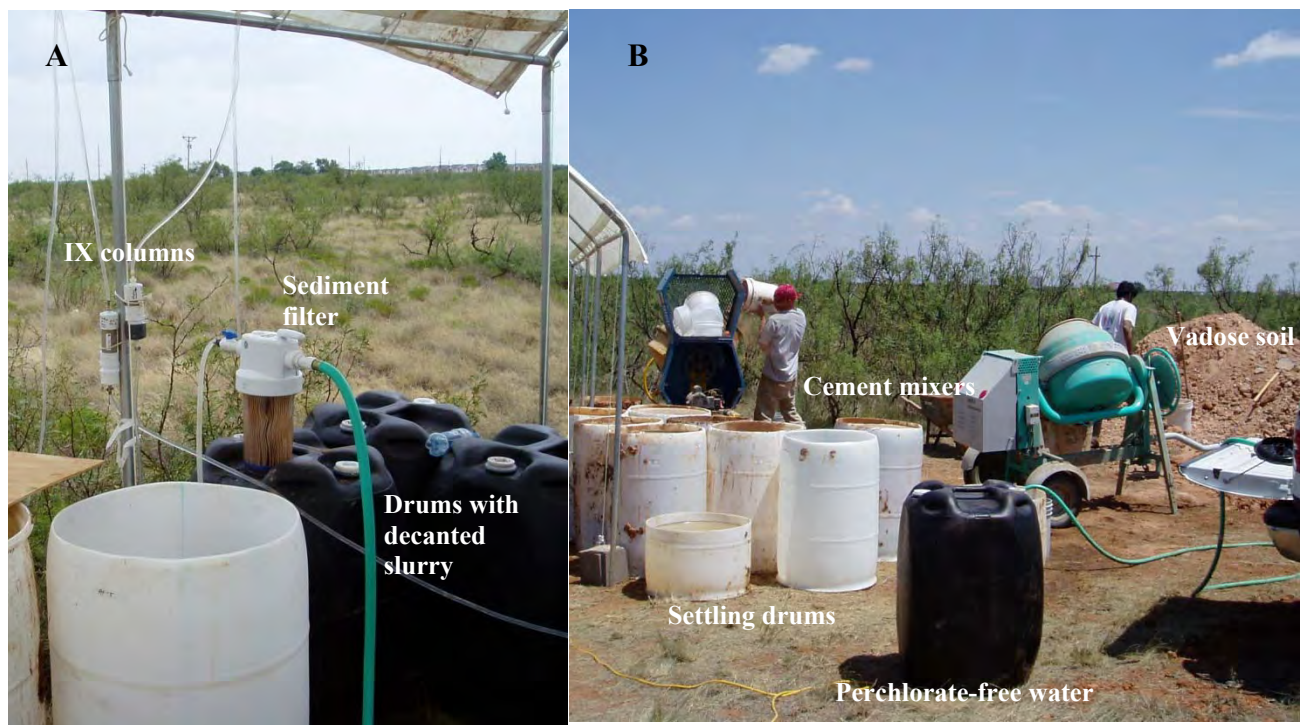
2.3 EXTRACTION AND PURIFICATION OF PERCHLORATE ON IX COLUMNS

2.3.1 Overview of Procedures

The second step after collection of ClO_4^- in the field is extraction of the adsorbed ClO_4^- from the IX resin and separation of the ClO_4^- from other compounds that also have some affinity to the IX resin, including nitrate (NO_3^-), sulfate (SO_4^{2-}), bicarbonate, (HCO_3^-), and a range of humic or other organic compounds and clays. Depending on the environmental source and location of the sample, other compounds, including perrhenate (ReO_4^-) and chlorate (ClO_3^-) may also be present on the resin and, in urban areas, surfactants and detergents commonly are adsorbed. A simple process utilizing ferric chloride ($FeCl_3$) and HCl has been developed to remove ClO_4^- from the bifunctional anion exchange resin, primarily by generating tetrachloroferrate ($FeCl_4^-$), which effectively displaces ClO_4^- on adsorption sites (Gu et al., 2001, 2007; Gu and Brown, 2006). However, the subsequent steps required to purify the extracted ClO_4^- from the complex mixture of residual $FeCl_3$, anions and organic compounds removed from the resin are both labor intensive and somewhat variable in nature depending on the anions and other chemicals in the extract. This phase of the process, which includes various precipitation, selective adsorption, and filtration steps has been the subject of significant research and development during the past few years. Additional development is ongoing as more difficult samples are processed (e.g., plant extracts, seawater, lake water, soils). The purification methods described in this section, which are current best practices, are likely to be refined and improved in the coming years.

2.3.2 Resin Removal from IX Columns and Resin Pre-Wash

The field sampling columns depicted in Figure 2.1 are compatible with the 4 M HCl used for resin extraction (as described in the next paragraph) provided that Teflon screens (rather than stainless steel) are used in construction. Direct extraction of these columns (with Teflon) to elute ClO_4^- is therefore possible without removing the resin. However, because the PVC IX columns are designed to process a large volume of water at a high flow rate, the initial step in ClO_4^- removal is generally to transfer the IX resin (with adsorbed ClO_4^-) from the field sampling column (Figures 2.1-2.3) into a preparative glass chromatography column (100 mL volume) fitted with Teflon end-plugs (e.g., Omnifit, Boonton, NJ, https://www.biochemfluidics.com/pdf/Columns.pdf). These chromatography columns can be tightly packed with the IX resin to ensure plug flow during extraction (and high washing efficiency) as settling of resin sometimes occurs in IX columns after field use. Multiple columns can be used if necessary (e.g., if a larger field resin column is used). To transfer the resin from a typical 100 mL field column, the screw-on end cap (Item F, Figure 2.1) should be unscrewed and the screen on top of the resin removed. The resin can then be carefully removed with a clean spatula and a small amount of water (or groundwater left in the column) and transferred to the glass preparative column. The glass columns should be labeled in accordance with accepted laboratory COC procedures. An intermediate step involving rinsing with ultrapure deionized water in an ultrasonic bath after removal from the field column and before transfer to the glass preparatory column may be advisable at this point if the resin exhibits a substantial discoloration or presence of fine sediment. Several rinses may be needed to obtain a clear rinse solution before proceeding to the glass preparative column.

After the resin has been packed into the glass preparatory column, it should then be washed with ~ 5 bed volumes (BV) of 4 M HCl. The HCl solution removes much of the adsorbed SO_4^{2-}, NO_3^-,

HCO_3^-, and some of the humics but does not desorb ClO_4^-, which is more strongly held by the bifunctional resin than most other anions or organics. A typical elution profile from a preparative column packed with resin is provided in Figure 2.5. It is clear in this figure that SO_4^{2-} ions elute quickly with nearly all SO_4^{2-} removed from the resin with only 1 BV of HCl solution. The NO_3^- desorbs more slowly, and small amounts are still observed in the effluent after leaching with 5 BV of the HCl solution. However, the process removes a majority of the NO_3^- on the IX resin column. The 4 M HCl also removes a significant fraction of the organics and carbonates when they are present on the resin. Although it is difficult to monitor for organics in the effluent solution, a brownish color of the initial solution eluting from the column is evidence of their presence in the HCl. Carbonates will be removed primarily as carbon dioxide (CO_2) gas evolution from the acidic solution. During the pre-wash, effluent samples should be collected and analyzed for ClO_4^- using one of the currently accepted methods (USEPA, 2009) to ensure that no significant loss occurs during the washing procedure. Analyses of other competing anions, such as SO_4^{2-} and NO_3^- can also be performed on effluent samples from the pre-wash using USEPA Method 300.0 (USEPA, 1993) to ensure adequate removal of these species.

Figure 2.5. Elution profiles of SO$_4^{2-}$, NO$_3^-$, and ClO$_4^-$ from IX columns using 4 M HCl as an extractant. The number of bed volumes of HCl is given on the x-axis.
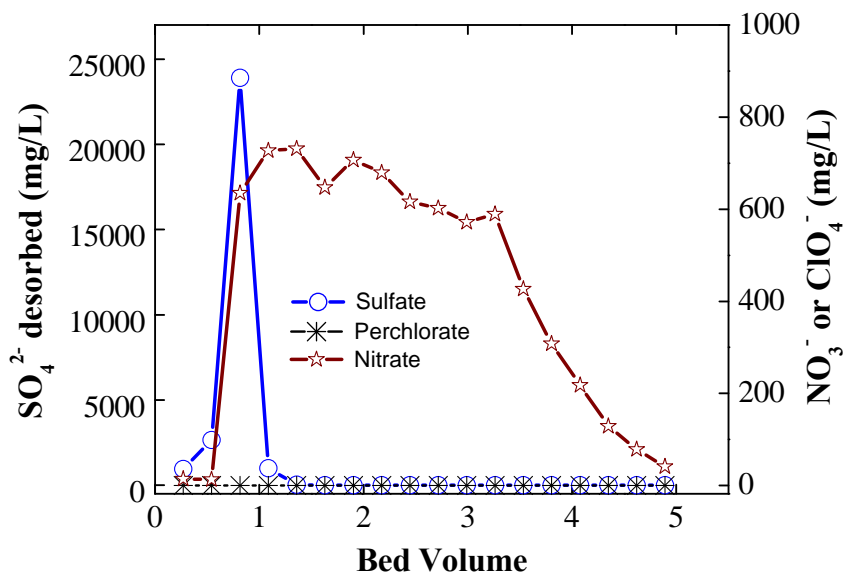
2.3.3 Perchlorate Elution and Analysis

The preparative column (Section 2.3.2) is next eluted with a combination of 1 M $FeCl_3$ and 4 M HCl to remove adsorbed ClO_4^- (Gu et al., 2001, 2007, 2011). When the $FeCl_3$ is mixed into an excess of Cl^-, $FeCl_4^-$ ions form at equilibrium according to Equation 2.2:

[Eq. 2.2] $FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^-$
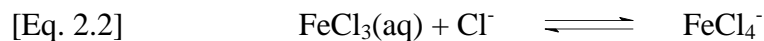
The $FeCl_4^-$ ion is chemically similar to ClO_4^-, each being large, poorly hydrated, tetrahedral anions. Because of their physicochemical similarities, $FeCl_4^-$ effectively displaces ClO_4^- from the bifunctional IX resin, and only a small number of bed volumes of the solution are required to completely desorb the resin-bound ClO_4^-. During the desorption process, two or more BV of the $FeCl_4^-$ solution should be run through the column and collected. Effluent may be collected at 0.1 to 0.25 BV intervals using a standard fraction collector with clean glass test tubes, and ClO_4^- concentration determined for each fraction. Because ClO_4^- elutes from the column as a sharp peak within ~ 1 BV (Figure 2.6), the total volume of eluent used for further ClO_4^- purification steps can be minimized by processing only the collected fractions containing ClO_4^-. The ClO_4^- concentration in each fraction of the effluent should be analyzed using USEPA Method 314.0 (USEPA, 1999) or an alternative accepted method (USEPA, 2009). The total amount of eluted ClO_4^- should then be determined using the concentration and volume of each fraction. The effluent fractions containing ClO_4^- should then be combined into a single sample for further processing, as described in the next section.

Figure 2.6. Elution of ClO_4^- from IX resin using $FeCl_4^-$ solution. The number of bed volumes of extractant is given on the x-axis.
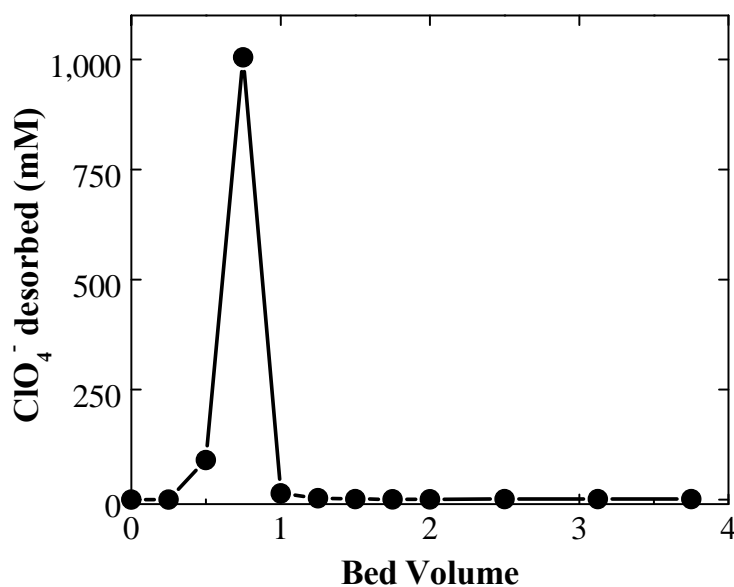
2.3.4 Effluent Cleanup and Concentration of Perchlorate

Two somewhat different approaches have been developed to recover ClO_4^- from the HCl-$FeCl_3$ eluent solution (Section 2.3.3). These alternative approaches, the first of which was developed at ORNL and the second at the University of Illinois at Chicago (UIC), utilize different techniques to remove abundant quantities of iron (Fe) (from the $FeCl_3$-HCl eluent) from solution. Each approach has advantages and disadvantages. Initial studies comparing the two approaches, which are described below, suggest that they provide comparable isotope data (unpublished data, ESTCP Project ER-200509). Additional development and verification work on these procedures is ongoing.

2.3.4.1 Iron Removal Using Neutralization and Precipitation

The raw eluent solution containing ClO_4^- also contains a high concentration of Fe, as well as a mixture of other anions and organics. A pure ClO_4^- salt must be obtained from this mixture. The ORNL approach to remove Fe and other impurities entails initial neutralization of the acidic eluent with sodium hydroxide (NaOH) in a glass beaker to achieve a pH between 9 and 10. At this alkaline pH, the Fe in solution precipitates primarily as iron (III) hydroxide ($Fe(OH)_3$) (red-brown precipitate) with the ClO_4^- remaining in the clear solution. The $Fe(OH)_3$ precipitates usually are separated by centrifugation at 6000 rpm for about 10 min, and clear supernatant solution is collected. The precipitates are washed once with deionized (DI) water, re-centrifuged, and clear supernatant solution is again collected (or combined). Alternatively the $Fe(OH)_3$ precipitates can be separated by filtration (0.45 μm) and washing with DI water under vacuum. The eluent is collected to recover ClO_4^-.

The resulting clear supernatant solution with ClO_4^- is then concentrated using a vacuum concentration system, such as a SpeedVac Concentrator (Savant Instruments, Holbrook, NY). The SpeedVac system centrifuges samples under vacuum to evaporate liquids. During evaporation, precipitates (mainly Na salts) should be removed periodically by filtration or by decanting the clear liquid away from them. The amount and type of precipitate will vary based on the impurities in each sample. The evaporative process should continue until the estimated ClO_4^- concentration in solution (based on estimates in the $FeCl_3$-HCl eluent) is in excess of 3 mg/mL. The degree of concentration required is based on the starting ClO_4^- concentration, and can exceed 100-fold for dilute solutions (i.e., due to low quantities of ClO_4^- on the resin). This high concentration of ClO_4^- is necessary to crystallize ClO_4^- salts in a final step (see Section 2.3.5). The concentration process can result in significant losses of ClO_4^-, particularly if large quantities of precipitate must be removed (as some ClO_4^- can be trapped in the precipitates or in liquid removed with the precipitates). The salts recovered during this process should be saved, and if losses of ClO_4^- are high, these salts can be re-dissolved in ClO_4^--free water. The resulting aqueous solution can then be passed over a small glass preparative column packed with Purolite A530E resin (e.g., 5 mL preparative column) to remove ClO_4^-. The ClO_4^- can then be desorbed from the resin and recovered using procedures described previously, beginning in Section 2.3.2. The resulting extract can be combined with the primary extract to increase the quantity of ClO_4^- recovered.

2.3.4.2 Iron Removal Using Ion Exchange

The second approach for ClO_4^- recovery, developed at UIC, utilizes cation exchange resin rather than pH adjustment to remove iron (III) (Fe^{3+}) ions from the column eluent. After evaluation of

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several different resins, Bio-Rad AG-50W-X12 resin, 100-200 mesh (Bio-Rad Co., Hercules, CA), was selected for this application. The main advantages of this protocol are that the Fe is removed without forming large quantities of $Fe(OH)_3$ precipitate and that large amounts of Na are not added. The main disadvantage of this process is the potential loss of ClO_4^- from adsorption onto the cation-exchange resin, despite the fact that both are negatively charged. Some resins can result in >35 % loss of ClO_4^-, thus the AG-50W-X12 resin is recommended for this application. Using this protocol, the $FeCl_3$-HCl eluent with dissolved ClO_4^- is passed through a large glass column packed with 600 mL of the AG-50W-X12 resin. The eluent is then collected and subjected to evaporation on a hot plate, with addition of 2 mL concentrated hydrogen peroxide (H_2O_2) to oxidize organic compounds, until 25 mL of solution remains (>3 mg/mL ClO_4^-). The evaporation of this azeotropic mixture (~6 M HCl) removes most of the excess HCl without any precipitation of sodium chloride (NaCl) or other Na salts. To separate residual NO_3^- from the ClO_4^-, the concentrated sample is reloaded onto 1 mL of A530E resin, flushed with 4 M HCl, re-eluted with $FeCl_3$-HCl, and the resulting eluent evaporated to <5 mL. The remaining excess dissolved Cl^- (HCl) is then removed by passing the sample through an OnGuard II silver (Ag) Sample Pretreatment Cartridge (Dionex, Sunnyvale, CA). OnGuard II H (cation-exchange hydronium form resin) cartridges are then used to remove any dissolved Ag^+. In unpublished tests from ESTCP ER-200509, the presence of Ag^+ was shown to fractionate oxygen isotopes during combustion (Section 2.4). The purity of the resulting ClO_4^- is evaluated by ion chromatography (IC) for the presence of other anions (see Section 2.3.6.2). At this stage, residual organics are removed by oxidation with pure H_2O_2 or by Strata SDB-L (Phenomenex, Torrance, CA) solid phase extraction.

2.3.5 Perchlorate Crystallization and Recovery

The final step in sample processing is crystallization of ClO_4^- as a salt. Prior to this step, it is important to check that no other precipitates are present in the final concentrated extract (>3 mg/mL ClO_4^-). If precipitates are observed, they should be removed via filtration. The concentrated ClO_4^- in the solution can be crystallized as rubidium perchlorate ($RbClO_4$) by adding rubidium chloride (RbCl), as cesium perchlorate ($CsClO_4$) by addition of cesium chloride (CsCl) or cesium hydroxide (CsOH), or as potassium perchlorate ($KClO_4$) by addition of potassium hydroxide (KOH) or potassium chloride (KCl). Most of the environmental samples for which published results are available have been prepared as $CsClO_4$ (See Appendix A, Table A-1), One approach to precipitate ClO_4^- as $CsClO_4$ (used at ORNL) is to add CsCl to ClO_4^--free water to form a saturated solution, and then add this solution dropwise to the clear extract with ClO_4^- to cause supersaturation (i.e., to form $CsClO_4$ precipitates). In general, a higher initial ClO_4^- concentration in the extract will yield higher recovery and more rapid precipitate formation. Theoretically, at a ClO_4^- concentration of 100 mg/mL, >99% of the ClO_4^- should precipitate as $CsClO_4$ salt compared to ~98% if KCl is used (Gu et al., 2011). Lower recovery may be observed when handling small volumes or lower concentrations of ClO_4^-. For example, at a ClO_4^- concentration of 5 mg/mL and a small volume (<1 mL), recoveries of <60% were observed in the laboratory (Gu et al., 2011). For this reason, it is important to collect as much ClO_4^- as possible during the sampling phase, as described in Section 2.2. The UIC procedure now exclusively precipitates $KClO_4$, to better match the $KClO_4$ isotopic reference materials, by adding an excess of KOH to the liquid sample after ion exchange cleanup (Section 2.3.4.2), and then to slowly evaporate the liquid. Residual KOH is removed from $KClO_4$ by rinsing the residue with methanol.

After crystallization of the ClO_4 salt is observed, the crystals should be collected by filtration, and the liquid saved and analyzed for residual ClO_4^-. The crystals should next be rinsed with a few drops of 90% methanol (by volume, in water) to ensure that surface of the crystallized ClO_4 salt is free from other salts. The salts should then be carefully collected and placed in a clean glass vial for assessment of purity, as described in Section 2.3.6.

2.3.6 Assessing Purity of Recovered Perchlorate Crystals

To ensure that the recovered $CsClO_4$ (or $KClO_4$) is of the highest purity for IRMS, the recovered ClO_4^- salts should be examined using one of two techniques: (1) nondestructive Raman spectroscopy or (2) dissolution and analysis by IC using USEPA Method 300.0 (USEPA, 1993) or equivalent. For large samples, both techniques can be used. Among the most common potential contaminants containing O are NO_3^- and SO_4^{2-}. ReO_4^- has also been identified in a subset of samples (Gu et al., 2011). It is desirable that impurities in the ClO_4^- salt comprise no more than 1% of the total O in the sample on a molar basis (i.e., the mole fraction [x] of O in the sample that is not attributable to ClO_4^- should be less than 0.01) in order to minimize any effects on O isotopic analysis. On a mass basis, this would correspond to approximately 0.02 mg of NO_3^- or 0.03 mg of SO_4^{2-} per mg of ClO_4^-. Organic compounds, including surfactants and humics, also are sometimes residual contaminants in purified samples if organic removal and oxidation steps are not 100% effective, particularly in samples from urban sources (surfactants) or surface-water samples and vadose-zone sediment extracts (humics). These compounds can react with oxygen gas (O_2) released during ClO_4^- decomposition, generating CO_2 and causing O isotopic fractionation. The CO_2 peak can be monitored when analyzing O_2 produced by ClO_4^- decomposition to determine the level of contamination with organic C, as described in Section 2.4. The impurity most likely to affect the Cl isotopic composition of recovered ClO_4^- is Cl^-. Chloride in solution during final precipitation of ClO_4^- salt by the ORNL method is efficiently excluded during the process, but care must be taken to ensure that residual Cl-rich liquid or NaCl is not included in the ClO_4^- product. The UIC method removes Cl^- prior to final precipitation of the ClO_4^- salt. Following either method, absence of Cl^- in the final product can be confirmed by IC.

2.3.6.1 Raman Spectroscopy

Micro-Raman spectroscopy is a nondestructive technique, which is advantageous for analyzing small samples (such as a single crystal) of $CsClO_4$ or $KClO_4$. The technique is commonly used to study vibrational frequency modes in a given molecule, and it relies on inelastic Raman scattering of monochromatic light, usually from a laser (Gu et al., 2009). The laser light interacts with molecules, resulting in the energy of the laser photons being shifted up or down, and this shift in energy gives information about the vibrational modes of the molecule. This Raman shift, which is characteristic of a pure compound, can thus be used to evaluate the purity of a solid, liquid, or gas using filters and a specialized detector (e.g., photodiode array detector). Background or inconsistent Raman shift patterns or peaks are indicative of impurities in a sample. Further details on Raman spectroscopy can be found in Smith and Dent (2005) and Gu et al. (2009).

To evaluate the purity of $CsClO_4$ (or $KClO_4$), Raman spectra should be collected from at least two to three single $CsClO_4$ crystals using a Raman Imaging Microscope and spectrometer. The

$CsClO_4$ crystals should exhibit needle-shaped morphologies, and they should have characteristic Raman bands at 937, 627, 460 cm^{-1}, respectively, the strongest band at about 937 cm^{-1} (Figure 2.7) (Gu et al., 2009, 2011). In addition, there are double bands at 1110 and 1085 cm^{-1}, a shoulder next to the 937 cm^{-1} band, and two minor bands between the 460 and 627 cm^{-1} bands. All of these bands should be present in the Raman spectra; any other peaks or peak shifts are indicative of impurities in the sample. Cubic or spherical shaped crystals usually indicate impurities such as NO_3^- or SO_4^{2-} salts, which can be detected by Raman spectroscopy with characteristic Raman shifts at 1050 cm^{-1} (for NO_3^-) and 980-985 cm^{-1} (for SO_4^{2-}), as shown in Figure 2.8. Pure $CsClO_4$ solids should exhibit smooth baselines (similar to the reagent $CsClO_4$ in Figure 2.7) with no visible Raman bands at 1050 or 980 cm^{-1}. At concentrations less than those illustrated in Figure 2.8, these impurities will have relatively little effect on the isotopic analysis of the $CsClO_4$. Broad and high background usually suggests the presence of impurities such as organics and other salts. In addition, as previously noted, a subset of samples from the Southwest has been observed to contain ReO_4^-, with visible spectral bands at 970 and 332 cm^{-1}. Rhenium (Re) is a very rare metal, but the most oxidized form, ReO_4^-, behaves similarly to ClO_4^-. Currently, the two anions cannot be separated, and samples with high ReO_4^- have not yet been analyzed for Cl and O isotopic composition. Thus far, substantial amounts of ReO_4^- have been found only in a few samples collected from mineral deposits in the Death Valley region; ReO_4^- was either absent, or present only at insignificant trace levels, in more than 100 other samples analyzed to date from other regions (Gu et al., 2011). Experiments are ongoing to determine methods to remove ReO_4^- from samples in which it occurs.

Figure 2.7. Raman sp ectrum of CsClO $_4$. Characteristic Raman bands are observed at 937, 627, 460 cm^{-1}.
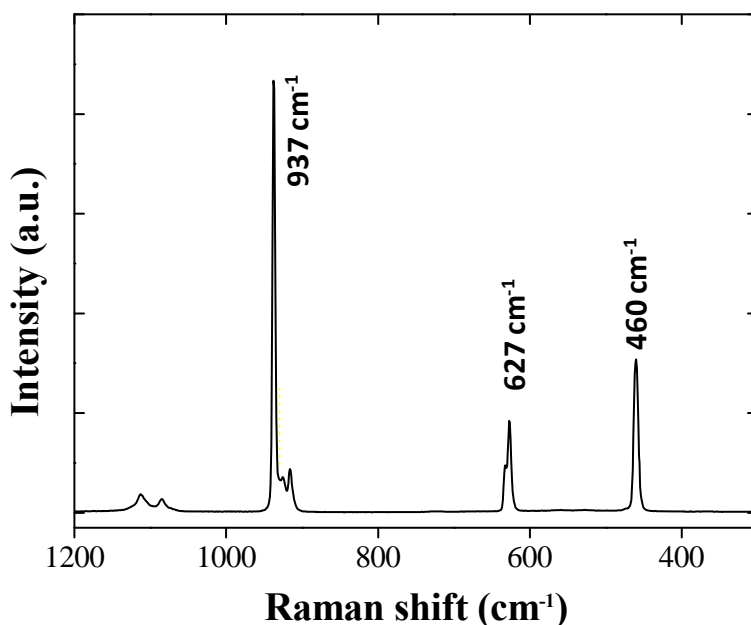
Figure 2.8. Raman spectra of CsClO$_4$ contaminated with ~0.3% NO$_3^-$, 1% SO$_4^{2-}$, or 1% ReO$_4^-$ (by mass) compared to pure CsClO$_4$. Corresponding mole fractions of O atoms from the contaminants in the mixtures are approximately 0.8%, 2.4%, and 0.9% for NO$_3^-$, SO$_4^{2-}$ and ReO$_4^-$, respectively. The broad and high background spectra as well as characteristic bands for NO$_3^-$, SO$_4^{2-}$, and ReO$_4^-$, respectively, reveal the presence of impurities in the sample. The y-axis is in relative arbitrary units (a.u.)
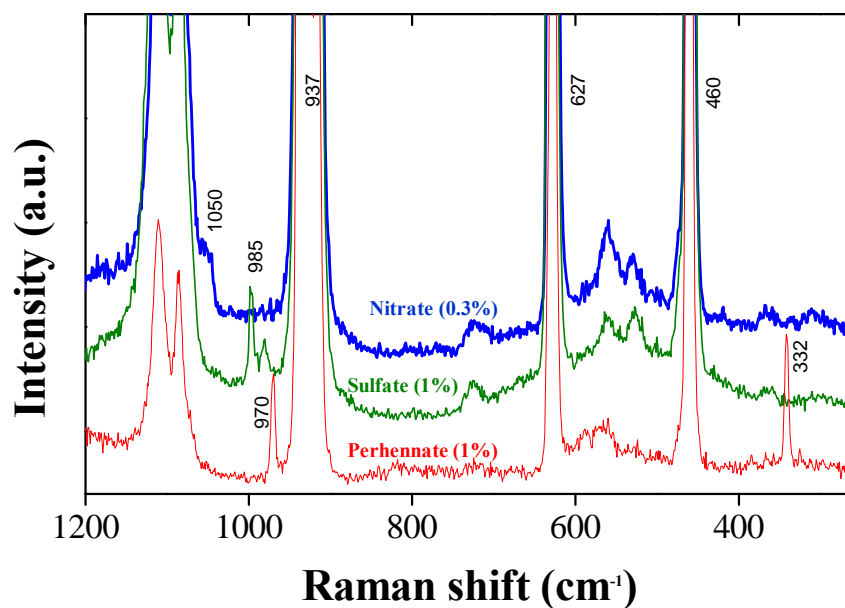
2.3.6.2 Ion Chromatography

If sufficient quantities of ClO_4^- are obtained during sample processing and purification, IC using USEPA Method 300.0 (USEPA, 1993) can be used to detect the most common impurities, including NO_3^- and SO_4^{2-}. However, this process is destructive, and a small quantity of the sample must be sacrificed. Various methods can be used for IC based on sample size. For large samples (>5 mg), ~1 mg of the $CsClO_4$ salt can be weighed and dissolved in 5 mL of DI water (volume required for typical IC analysis), which will result in a ClO_4^- concentration of ~85 mg/L. The presence of 0.8% NO_3^- and 1.0% SO_4^{2-} by mass, which is equivalent to a mole fraction of O of ~0.01 from these impurities (where mole fraction of O from impurity is [mol O from impurity]/[mol O from ClO_4^- plus impurity]), would result in concentrations of ~0.70 and 0.85 mg/L of each, respectively, which are readily detectable by USEPA Method 300.0 (method detection limit [MDL] for each of these anions is ~0.1 to 0.2 mg/L). A typical chromatograph for USEPA Method 300.0 with all constituents at 0.2 mg/L is shown in Figure 2.9. As observed in the figure, other oxygen-containing species including phosphate (PO_4^{2-}), ClO_3^-, and nitrite (NO_2^-) can also be detected by this method, as well as Cl^-. ClO_4^- is not detected by USEPA 300.0 and should be analyzed by USEPA 314.0 or equivalent. For small samples (i.e., <5 mg), the entire processed sample (or a portion sufficiently large weighed accurately) can be dissolved in DI water to give a final concentration of ~0.3-0.6 mg/mL as ClO_4^-, and then a 200-µL aliquot of that aqueous sample (~60-120 µg ClO_4^-) can be dissolved in DI water and analyzed by IC. The technique will again provide the required MDL 0.1 to 0.2 mg/L of each potential contaminating anion required to evaluate purity at the level of 0.01 mole fraction of contaminant O.

Figure 2.9. Typical ion chromatogram from   USEPA Method 300.0 for various anions at concentrations of approximately 0.2 mg/L in an aqueous sample.

Sample Run ID:	0.2ppm		Sample No.:	4
Sample ID:			Sequence Name:	10-21-10B ANIONS
Program Method:	EPA 300 KOH		Injection vol.:	25.0
Quantitation Method:	EPA300(KOH)		Dilution Factor:	1.0000
Date Time Collected:	10/22/2010 10:45 AM		Sample Wt.:	1.0000
System Operator:	randi.rothmel		Sample Amt.:	1.0000

Peak No.	Component Name	Retention Time	Area µS*min	Height µS	Amount ppm	Amnt.Dev.(rel) %	Relative Amount %
1	flouride	4.15	0.082	0.407	0.1822	-8.8981	12.16
n.a.	Chlorite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Chloride	5.90	0.045	0.261	0.1800	-10.0196	12.01
3	Nitrite	7.14	0.115	0.530	0.2030	1.5185	13.55
4	Sulfate	8.13	0.037	0.145	0.1762	-11.8839	11.76
5	Bromide	10.16	0.018	0.067	0.1551	-22.4462	10.35
6	Nitrate	12.02	0.111	0.348	0.1786	-11.7093	11.79
7	Chlorate	13.08	0.017	0.047	0.1576	-21.2097	10.52
8	Phosphate	16.23	0.069	0.117	0.2675	33.7419	17.85

10-21-10B ANIONS #4 [modified by randi.rothmel]   ECD_1

30
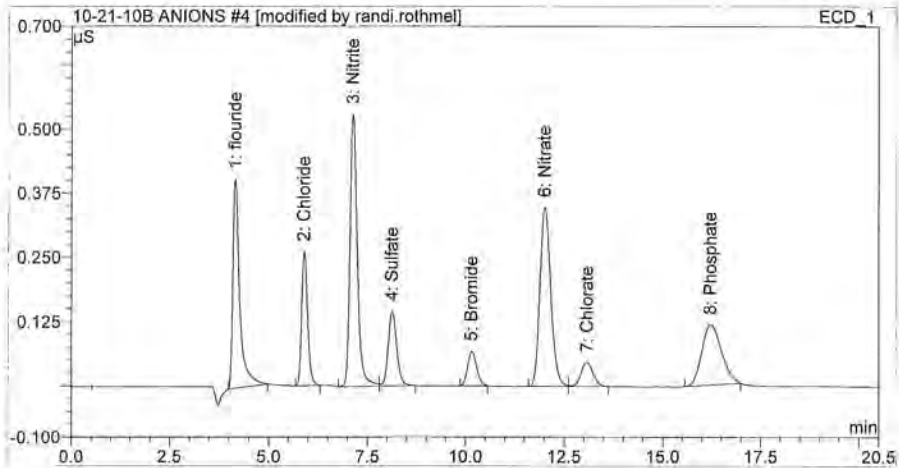
2.3.7 Reprocessing Impure Samples

If impurities are identified in a purified sample of $CsClO_4$ (or $KClO_4$) by Raman spectroscopy or IC at concentrations appreciably greater than 1% of the total O in the sample on a molar basis (as described in Section 2.3.6), the sample may be further purified by redissolving in ClO_4^- -free distilled deionized (DDI) water, reprecipitating by evaporation, and rinsing with a small amount (e.g., 1 drop) of methanol or H_2O_2 solution, until satisfactory purity is achieved. In some instances, depending on the type of contaminant, it may be beneficial to pass the aqueous solution with ClO_4^- thorough a small (e.g., 5-mL volume) glass preparative column with A530E resin so that the ClO_4^- is selectively adsorbed in the resin. The resin can then be reprocessed by washing with HCl to remove impurities, as described in Section 2.3.2. The ClO_4^- should then be eluted and purified, as described in Sections 2.3.2 – 2.3.6. The samples may have to be reprocessed more than once if elevated levels of impurities are detected, which is most common for samples obtained from soils, mineral extracts, or surface water bodies (e.g., Great Lakes; ESTCP Project ER-200509, unpublished data). When impurities are detected at concentrations corresponding to <0.01 for the mole fraction of O in the sample by Raman spectroscopy and (or) IC, the sample is ready for Cl and O isotopic analyses by IRMS, as described in Sections 2.4 and 2.5, respectively.

2.3.8 QA/QC Considerations for Perchlorate Elution and Purification

A summary of relevant QA/QC considerations for ClO_4^- elution and purification is provided in this section.

The following QA/QC procedures are recommended:

1. All chemicals used for washing and resin regeneration (e.g., HCl, NaOH, and $FeCl_3$) should be of analytical reagent grade and ClO_4^--free.

2. Water used to make solutions should be tested to be ClO_4^--free (<0.1 µg/L) or passed through A530E IX resin prior to use to remove ClO_4^-.

3. Use of reagent blanks is recommended during sample processing.

4. All containers to which an individual sample is transferred should be properly labeled and documented according to established laboratory COC procedures.

5. An unused IX resin column (Equipment Blank), as described in Section 2.2.6, or a sample of virgin A530E resin can be processed with field samples to ensure that there is no contamination with ClO_4^- during sample collection, shipping, or processing. ClO_4^- should not be detected at any time in samples prepared from the field blank or unused resin at amounts >10 µg/60 g dry mass.

6. An internal control sample can be prepared in the laboratory by dissolving 10 mg of $KClO_4$ or sodium perchlorate ($NaClO_4$) salt with a known isotopic composition in 1 L of DI water, and passing that water through an IX resin column to trap the dissolved ClO_4^-. This column can then be processed with the field sample columns from a site. The O and Cl isotopic composition of ClO_4^- from the control column should be the same as that of the parent salt ($\pm$

expected analytical variability). Any isotopic fractionation due to sample processing (e.g., due to precipitation) can be documented in this way, and corrections can be made to field samples if required.

7. Raman Reference Standards: Reagent $CsClO_4$ and/or $KClO_4$ should be used as a reference standard for Raman analysis, matching the final form of the field samples.

8. Typical standards and blanks for USEPA Methods 300.0 and 314.0 should be analyzed as described previously (USEPA, 1993).

2.4 ANALYSIS OF OXYGEN ISOTOPES IN PERCHLORATE BY IRMS

After the $CsClO_4$, $RbClO_4$, or $KClO_4$ is purified according to the procedures described in Section 2.3, it is analyzed for O and Cl isotopic composition by IRMS according to the procedures described in Section 2.4 (this section) for O and Section 2.5 for Cl. Abbreviated descriptions of methods and calibrations of O isotopic analyses have been published previously in several papers and book chapters as described in Section 2.1. Additional publications describing the procedures used for production and calibration of ClO_4^- isotopic reference materials, along with additional information about analytical methods, are in preparation. The current summary, therefore, represents the current state of the art, but is subject to modifications or updates in the future.

Analysis of O isotopes in ClO_4^- can be conducted by two different methods, both of which are described in the following sections. The first method entails conversion of alkali perchlorate salts to alkali chloride salts plus O_2 gas. The values of $\delta^{18}O$ and $\delta^{17}O$ can each be measured by decomposing $CsClO_4$ (or $RbClO_4$ or $KClO_4$) to yield a stoichiometric quantity of O_2 according to the reaction:

$$CsClO_4 \rightarrow CsCl + 2O_2$$
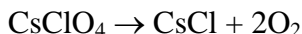
The O_2 gas is then admitted to a magnetic-sector type, dual-inlet isotope-ratio mass spectrometer (DI-IRMS) and analyzed by monitoring mass-to-charge ratio (m/z) 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), and 34 ($^{18}O^{16}O$, plus an insignificant contribution from $^{17}O^{17}O$). Yields of O (as O_2) by this method are typically within $\pm 5\%$ for pure ClO_4^- salts. Method details and QA/QC considerations are provided in Section 2.4.2. Analysis of $\delta^{18}O$ (but not $\delta^{17}O$) also can be done by reacting the ClO_4^- salt with glassy C to produce carbon monoxide (CO), which is then transferred in a helium (He) carrier through a molecular-sieve to a continuous-flow IRMS (CF-IRMS) and analyzed by monitoring peaks at m/z 28 ($^{12}C^{16}O$) and 30 ($^{12}C^{18}O$, plus an insignificant contribution from $^{13}C^{17}O$). Yields of O (as CO) typically are 100 $\pm 2\%$ for pure ClO_4^- reagents and samples. Method details and QA/QC considerations are provided in Section 2.4.3.

2.4.1 Terminology and Standards for Oxygen Stable Isotopic Analysis
As described in Section 1.3, stable isotopic compositions are measured and reported as relative differences of isotope ratios (in either moles or numbers of atoms) between two substances, one of which may be an international measurement standard (Equation 2.1). For oxygen:

[Eq. 2.3] $\delta^{18}O = R(^{18}O/^{16}O)_{sample}/R(^{18}O/^{16}O)_{standard} - 1$

[Eq. 2.4] $\delta^{17}O = R(^{17}O/^{16}O)_{sample}/R(^{17}O/^{16}O)_{standard} - 1,$

where the standard in both equations is VSMOW. Values of $\delta^{18}O$ and $\delta^{17}O$ typically are reported in parts per thousand (or ‰). By international convention, the $\delta^{18}O$ scale is defined by two standards, with VSMOW at 0 and Standard Light Antarctic Precipitation (SLAP) at a value of -55.5‰ (Gonfiantini, 1978; Coplen, 1994).

Variations in $R(^{17}O/^{16}O)$ and $R(^{18}O/^{16}O)$ caused by most physical-chemical fractionation processes on Earth are related systematically by the relative differences in the masses of the isotopes. Such "mass-dependent" variations can vary slightly for different processes and they can be described in various ways (e.g., Thiemens, 1999; Miller, 2002; Angert et al., 2004; Assonov and Brenninkmeijer, 2005). In this report:

[Eq. 2.5] $(1 + \delta^{17}O) = (1 + \delta^{18}O)^{\lambda},$

with $\lambda \approx 0.525$ (Miller, 2002; Böhlke et al., 2005). Departures from mass-dependent O-isotope variation are important features of some materials, including some natural ClO_4^-. Departures from mass-dependent O-isotope variation in ClO_4^- are described in this report as deviations from the relation given in Equation 2.5:

[Eq. 2.6] $\Delta^{17}O = [(1 + \delta^{17}O) / (1 + \delta^{18}O)^{0.525}] - 1.$

Values of $\Delta^{17}O$ typically are reported in parts per thousand (or ‰).

Because water (H_2O) samples may not be compatible with analytical techniques used for other compounds such as ClO_4^-, Equations 2.3 and 2.4 are expanded to permit routine calibration of ClO_4^- analyses using a pair of ClO_4^- isotopic reference materials (USGS37 and USGS38) with contrasting isotopic compositions on the VSMOW-SLAP scale, a process commonly referred to as "normalization":

[Eq. 2.7] $\delta^{18}O_{i/VSMOW} = \delta^{18}O_{37/VSMOW} +$
$[\delta^{18}O_{i/rg} - \delta^{18}O_{37/rg}]_{meas.} \cdot [\delta^{18}O_{38/VSMOW} - \delta^{18}O_{37/VSMOW}] / [\delta^{18}O_{38/rg} - \delta^{18}O_{37/rg}]_{meas.}$

[Eq. 2.8] $\delta^{17}O_{i/VSMOW} = \delta^{17}O_{37/VSMOW} +$
$[\delta^{17}O_{i/rg} - \delta^{17}O_{37/rg}]_{meas.} \cdot [\delta^{17}O_{38/VSMOW} - \delta^{17}O_{37/VSMOW}] / [\delta^{17}O_{38/rg} - \delta^{17}O_{37/rg}]_{meas.},$

where 37 and 38 refer to the ClO_4^- reference materials USGS37 and USG38, and rg is an internal laboratory reference gas (either CO or O_2, see below) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses.

The isotopic reference materials consist of reagent-grade $KClO_4$ salts that were prepared specifically for calibration of ClO_4^- isotopic analyses as part of ESTCP Project ER-200509. The $\delta^{18}O$ scale is based on CO-CF-IRMS analyses (see below) of the ClO_4^- isotopic reference materials against international H_2O, NO_3^-, and SO_4^{2-} isotopic reference materials as described by Böhlke et al. (2003), and all data are referenced to the conventional VSMOW-SLAP scale

(Gonfiantini, 1978; Coplen, 1994). For $\delta^{18}O$, the secondary calibration values used to generate provisional ClO_4^- data with respect to VSMOW are -27.9‰ for USGS34 (potassium nitrate [KNO_3]), +25.6‰ for IAEA-N3 (KNO_3), +57.5‰ for USGS35 ($NaNO_3$), and +8.6‰ for NBS 127 (barium sulfate [$BaSO_{4]}$]) (Böhlke et al., 2003). The $\delta^{17}O$ scale for ClO_4^- is provisionally based on the assumption that the normal reagent $KClO_4$ reference material (USGS37) has $R(^{17}O/^{16}O)$ and $R(^{18}O/^{16}O)$ values that are related to those of VSMOW by mass-dependent processes ($\Delta^{17}O=0$, as defined by Equation 2.6; Böhlke et al., 2005).

International efforts to reconcile $\delta^{18}O$ calibration scales for different reference materials are ongoing in the scientific community (e.g., Brand et al., 2009), as are efforts to define and calibrate mass-dependent variations in $\delta^{18}O$ and $\delta^{17}O$ for different chemical systems and processes. The current project (ESTCP ER-200509) is contributing to these efforts, while providing an interim basis for reporting and comparing O isotope data for environmental samples of ClO_4^-. Because the calibration data are provisional and could change, reported data are accompanied by descriptions of the reference materials and calibration values that were used during the analyses, and by the equations that were used to evaluate mass dependence, to permit subsequent re-evaluation and comparison with other data.

2.4.2 Analysis of $\delta^{18}O$ and $\delta^{17}O$ by Off-Line Conversion to O_2, with Dual-Inlet Isotope-Ratio Mass Spectrometry (O_2-DI-IRMS)

To perform DI-IRMS on O_2 derived from ClO_4^-, aliquots of pure $CsClO_4$, $RbClO_4$, or $KClO_4$, including reagents and environmental samples derived from the sampling and purification methods described previously in Sections 2.2 and 2.3 of this document, are weighed into quartz glass tubes (mass equivalent to 2.5 µmol of ClO_4^- per tube). The tubes are evacuated and sealed with a torch and baked at 650 °C for 20 min to produce O_2 gas from the ClO_4^-. Alternatively, samples are weighed into Pyrex glass tubes (mass equivalent to 2.5 µmol of ClO_4^- per tube), which are evacuated and sealed with a torch, and baked at 600 °C for 30 min to produce O_2 gas. The tubes are broken manually in an evacuated glass tube cracker, the O_2 is expanded into a liquid N_2 cold trap for 1 min to remove traces of condensable gases (except when being tested for other decomposition products such as CO_2), then admitted to an IRMS and analyzed in dual-inlet mode against an O_2 reference gas from a tank by monitoring m/z 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), and 34 ($^{18}O^{16}O$, plus an insignificant contribution from $^{17}O^{17}O$).

The following routine QA/QC checks for DI-IRMS analysis of O_2 are recommended:

1. Aliquots of samples and reference materials must yield constant amounts of O_2 to provide optimum conditions and minimize bias in mass spectrometry (Werner and Brand, 2001). Masses of samples and reference materials should be adjusted to yield constant amounts of O_2 (typically within ±10% or less within a batch); masses should be recorded to permit subsequent yield calculations.

2. The vacuum system used to seal the tubes should be evaluated by an electronic gauge, and tubes should be sealed only if the reading is stable at a level that produces negligible O_2 blanks (this can be tested periodically by analyzing empty sealed tubes in the mass spectrometer).

3. The relative amount of O_2 released from each tube (sample yield) should be measured in the IRMS and compared to the expected amount based on the measured weight of the sample in comparison to yields from pure reagents; if a yield is substantially different, the analysis should be flagged for attention. This represents an additional QC check for sample purity, in addition to those described in Section 2.3.6.

4. The relative amounts of N_2, Ar, and CO_2 (potentially indicating air leakage or other contamination) associated with O_2 samples should be measured in the IRMS; if any are substantially higher than normal mass spectrometer blanks, the analysis should be flagged for attention (e.g., considered for rejection if other analyses of the same sample are systematically different).

5. Isotopic reference materials should be prepared and analyzed as samples (multiple aliquots) with every batch of samples being analyzed (Werner and Brand, 2001). A normal batch consists of about 10 to 20 samples and reference materials, all prepared identically and analyzed on the same day. For the reference materials, standard deviations of $\delta^{18}O$ analyses of multiple aliquots (typically three to four) in a given batch generally are around ±0.2‰ or better for USGS37 and ±0.5‰ or better for USGS38; if substantially larger, then   the analyses should be flagged for attention (e.g., considered for rejection if other analyses of the same samples are systematically different).

6. With few exceptions, such as when sample amounts are limited, samples should be analyzed at least twice in different batches on different days to minimize bias related to daily calibrations. The stated uncertainties of sample analyses are based on these replicates.

2.4.3 Analysis of $\delta^{18}O$ by On-Line Conversion to CO, with Continuous-Flow Isotope-Ratio Mass Spectrometry (CO-CF-IRMS)

To perform CF-IRMS on CO derived from ClO_4^-, aliquots of pure $CsClO_4$, $RbClO_4$, or $KClO_4$, including reagents and environmental samples derived from the sampling and purification methods detailed previously in Sections 2.2 and 2.3 of this document, are weighed into silver foil cups (mass equivalent to 2 µmol of ClO_4^- per cup). The loaded cups are dropped automatically from a He-flushed carousel into a graphite crucible in a glassy carbon reactor at a nominal (gauge) temperature of 1325 °C to produce CO gas from the ClO_4^-. The CO is transferred in He carrier gas through a molecular-sieve gas chromatograph to an IRMS and analyzed in continuous-flow mode by monitoring peaks at m/z 28 ($^{12}C^{16}O$) and 30 ($^{12}C^{18}O$, plus an insignificant contribution from $^{13}C^{17}O$).

The following routine QA/QC checks for CF-IRMS of CO are recommended:

1. Aliquots of samples and reference materials should yield constant amounts of CO to provide optimum conditions and minimize bias in mass spectrometry. Masses of samples and reference materials should be adjusted to yield constant amounts of CO (typically within ±5% or less within a batch); masses should be recorded to permit subsequent yield calculations.

2. The relative amount of CO released from each aliquot (sample yield) should be measured in the mass spectrometer and compared to the expected amount based on the measured mass of

the sample in comparison to yields from pure reagents; if a yield is substantially different, the analysis should be flagged for attention.

3. The relative amount of N_2 (potentially indicating air leakage or other contamination, such as NO_3^-) in each sample should be measured in the IRMS by monitoring *m/z* 28 throughout the continuous-flow run from the gas chromatograph (GC) (the $^{14}N^{14}N$ peak precedes the $^{12}C^{16}O$ peak). Typically, the area of the $^{14}N^{14}N$ peak is negligible; if not, the analysis should be flagged for attention.

4. Isotopic reference materials should be prepared and analyzed as samples (multiple aliquots) with every batch of samples being analyzed. A typical normal batch consists of about 30-50 samples and reference materials, all analyzed in the same run within a 24-hour period. For the reference materials, standard deviations of $\delta^{18}O$ analyses of multiple aliquots (typically four to eight) in a given batch generally are around ±0.2‰ or better for USGS37 and ±0.2‰ or better for USGS38; if substantially larger, the analysis should be flagged for attention.

5. With few exceptions, such as when samples are limited), samples should be analyzed at least twice in different batches on different days, to minimize bias related to daily calibrations. The stated uncertainties of sample analyses are based on these replicates.

2.5 ANALYSIS OF CHLORINE ISOTOPES IN PERCHLORATE BY ISOTOPE-RATIO MASS SPECTROMETRY

The analysis of Cl stable isotopes is conducted on the Cl^- produced by decomposition of alkali ClO_4^- salts, as described in Section 2.4 for production of O_2. The Cl^- derived from ClO_4^- initially is converted to methyl chloride (CH_3Cl) gas by reaction of silver chloride (AgCl) with methyl iodide (CH_3I) (Eggencamp, 1994; Holt et al., 1997), which is then analyzed by IRMS according to the procedures described in this section. The methods and calibrations of Cl isotopic analyses from ClO_4^- have been summarized previously in several papers and book chapters, as described in Section 2.1.

2.5.1 Terminology and Standards for Chlorine Stable Isotopic Analysis

As described in Section 1.3, stable isotopic compositions are measured and reported as relative differences of isotope ratios (in either moles or numbers of atoms) between two substances, one of which may be an international measurement standard (Equation 2.1). For chlorine:

[Eq. 2.9] $\qquad \delta^{37}Cl \ = \ R(^{37}Cl/^{35}Cl)_{sample} \ / \ R(^{37}Cl/^{35}Cl)_{standard} - 1$

where the international measurement standard is SMOC. Values of $\delta^{37}Cl$ typically are reported in parts per thousand (or ‰). The most widely-used Cl isotope reference material is chloride prepared from seawater, which has uniform $\delta^{37}Cl$ to within ±0.08‰ (Godon et al., 2004).

Routine calibration of ClO_4^- isotopic analyses can be done by using a pair of ClO_4^- isotopic reference materials (USGS37 and USGS38) with contrasting isotopic compositions, a process commonly referred to as "normalization":

[Eq. 2.10] $\qquad \delta^{37}Cl_{i/SMOC} \ = \ \delta^{37}Cl_{37/SMOC} +$

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$[\delta^{37}Cl_{i/rg} - \delta^{37}Cl_{37/rg}]_{meas.} \cdot [\delta^{37}Cl_{38/SMOC} - \delta^{37}Cl_{37/SMOC}] / [\delta^{37}Cl_{38/rg} - \delta^{37}Cl_{37/rg}]_{meas.}$

where 37 and 38 refer to the perchlorate isotopic reference materials USGS37 and USG38, and rg is an internal laboratory reference gas (CH_3Cl) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses.

Isotopic reference materials consist of reagent-grade $KClO_4$ salts that were prepared specifically for calibration of ClO_4^- isotopic analyses, as described in Section 2.4.1. The $\delta^{37}Cl$ scale is based on isotopic analyses of the USGS perchlorate isotopic reference materials against SMOC. As noted for O isotopes in ClO_4^-, the current ClO_4^- isotope project (ESTCP ER-200509) is providing an interim basis for reporting and comparing Cl isotope data for environmental samples of ClO_4^-. Because the calibration data are provisional and could change, reported data are accompanied by statements describing the normalization equations and values that were used during the analyses to permit subsequent re-evaluation.

2.5.2 Analysis of $\delta^{37}Cl$ by Off-Line Conversion to Methyl Chloride, with Dual-Inlet Isotope-Ratio Mass Spectrometry (CH_3Cl-DI-IRMS)

Chlorine isotopic analyses are performed on samples of alkali halide (CsCl, RbCl, or KCl) residues from decomposition of ClO_4^- salts as described above for preparation of O_2 for isotopic analysis (Section 2.4.2). Alkali halide residue in a decomposition tube is dissolved using 10 mL of warm 18.2 megohms ($M\Omega$) deionized water. The dissolved alkali halide residue is transferred into a 50-mL polypropylene conical tube. Sodium phosphate/citric acid buffer (0.004 M phosphate, 0.098 M citric acid) and potassium nitrate (0.4 M KNO_3) are added to optimize crystallization of AgCl in the subsequent step. This solution is then heated to 80 °C and an excess of silver nitrate ($AgNO_3$) is added, as described in Eggenkamp (1994). AgCl precipitates are then allowed to ripen in the dark for ~24 hr. The AgCl solids are then centrifuged, the supernatant is removed, and dilute 0.03 M nitric acid (HNO_3) is used to rinse the solids three times. Solids are then transferred into a Pyrex combustion tube (20 cm x 9 mm) and dried in a darkened vacuum oven at 80 °C. After the sample is dry, the combustion tube is evacuated and CH_3I is cryogenically transferred into the tube, which is then sealed and baked for 2 h at 300 °C, as described in Holt et al. (1997). The resulting CH_3Cl is purified using gas chromatography, cryo-concentrated, and then admitted to an IRMS and analyzed in dual-inlet mode by monitoring peaks at m/z 52 ($^{12}C^1H_3^{37}Cl$) and 50 ($^{12}C^1H_3^{35}Cl$). Samples smaller than 5 µmol of Cl (0.5 mg ClO_4^-) can be analyzed by CF-IRMS, as described in Section 2.5.3.

The following routine QA/QC checks for DI-IRMS analysis of Cl are recommended:

1. Preparation of every batch of 10-15 samples should include the concurrent preparation of two different USGS perchlorate isotopic reference materials (USGS37 and USGS38), as described previously. Seawater chloride samples should also be analyzed with each batch to monitor instrument performance and stability.

2. Aliquots of samples and reference materials must yield constant amounts of Cl to provide optimum conditions and minimize bias in mass spectrometry. Masses of samples and reference materials should be adjusted to yield constant amounts of Cl (typically within ±5% or less within a batch); masses should be recorded to permit subsequent yield calculations.

3. The vacuum system used to seal the tubes should be evaluated by an electronic gauge, and tubes sealed only if the reading is stable at a level that produces negligible CH_3Cl blanks (tested periodically by analyzing empty sealed tubes in the mass spectrometer).

4. The relative amount of CH_3Cl released from each tube (sample yield) should be measured in the IRMS and compared to the expected amount based on the measured mass of the sample, in comparison to yields from pure reagents; if a yield is substantially different, the analysis should be flagged for attention.

5. The relative amounts of nitrogen gas (N_2), argon (Ar), and CO_2 (potentially indicating air leakage or other contamination) in each CH_3Cl aliquot are measured in the IRMS; if any of these are substantially higher than normal mass spectrometer blanks, the analysis should be flagged for attention.

6. Isotopic reference materials should be prepared and analyzed as samples (multiple aliquots) with every batch of samples being analyzed. A normal batch consists of about 10 to 20 samples and reference materials, all analyzed on the same day. For the reference materials, standard deviations of $\delta^{37}Cl$ analyses of multiple aliquots generally are around ±0.2‰ or better for USGS37 and ±0.3‰ or better for USGS38; if substantially larger, the analysis should be flagged for attention.

7. With few exceptions, such as when samples amounts are limited, samples should be analyzed at least twice in different batches on different days to minimize bias related to daily calibrations. The stated uncertainties of sample analyses are based on these replicates.

2.5.3 Analysis of $\delta^{37}Cl$ by On-Line Separation of Methyl Chloride, with Continuous-Flow Isotope-Ratio Mass Spectrometry (CH_3Cl-CF-IRMS)

Small samples (<5 µmol of Cl in CH_3Cl) can be analyzed for Cl isotopic composition by CF-IRMS rather than DI-IRMS (Section 2.5.2). The same general sample preparation techniques are used as described in Section 2.5.2 until the final steps. The reacted CH_3Cl/CH_3I mixture is transferred in a He carrier-gas through a molecular-sieve gas chromatograph to separate CH_3Cl from CH_3I, then the He carrier-gas is admitted to an IRMS and the Cl isotope ratio analyzed in continuous-flow mode by monitoring peaks at m/z 52 ($^{12}C^1H_3{}^{37}Cl$) and 50 ($^{12}C^1H_3{}^{35}Cl$).

The following routine QA/QC checks are recommended for Cl isotopic analysis by CH_3Cl-CF-IRMS:

1. Preparation of every batch of 10-15 samples should include the concurrent preparation of two different USGS perchlorate isotopic reference materials, as described previously. Seawater chloride samples should also be analyzed with each batch to monitor instrument performance and stability.

2. Aliquots of samples and reference materials must yield constant amounts of Cl to provide optimum conditions and minimize bias in mass spectrometry. Masses of samples and

reference materials should be adjusted to yield constant amounts of Cl (typically within ±5% or less within a batch); masses should be recorded to permit subsequent yield calculations.

3. The relative amounts of N_2, Ar, and CO_2 (potentially indicating air leakage or other contamination) in each CH_3Cl aliquot are measured in the IRMS; if any are substantially higher than normal mass spectrometer blanks, the analysis should be flagged for attention.

4. Isotopic reference materials should be prepared and analyzed as samples (multiple aliquots) with every batch of samples being analyzed. A normal batch consists of about 10-20 samples and reference materials, all analyzed on the same day. For the reference materials, standard deviations of $\delta^{37}Cl$ analyses of multiple aliquots generally are around ±0.2‰ or better for USGS37 and ±0.5‰ or better for USGS38; if substantially larger, the analysis should be flagged for attention.

5. With few exceptions, such as when samples amounts are limited), samples should be analyzed at least twice in different batches on different days to minimize bias related to daily calibrations. The stated uncertainties of sample analyses are based on these replicates.

2.6 ANALYSIS OF ^{36}Cl FROM PERCHLORATE

Chlorine-36 (^{36}Cl) is a long-lived radioactive isotope of Cl with a half-life of ~301,000 yr. The abundance of ^{36}Cl in a sample traditionally is expressed as ^{36}Cl/Cl, which is equivalent to the atom fraction or mole fraction of ^{36}Cl, $x(^{36}$Cl), or $N(^{36}$Cl)/$N(\Sigma$Cl). Meteoric water has an average natural ^{36}Cl/Cl value of approximately 700×10^{-15} (Bentley et al., 1986; Phillips, 2000; Davis et al., 2003). ^{36}Cl is formed primarily in the stratosphere through the cosmic ray spallation of ^{40}Ar (Lehmann et al., 1993). This radioactive isotope is of interest for forensic analysis of ClO_4^- because recent data indicate that it is significantly enriched in natural indigenous ClO_4^- samples collected from the southwestern United States (^{36}Cl/Cl values ranging from 3130×10^{-15} to $28,800 \times 10^{-15}$) compared to either synthetic samples (^{36}Cl/Cl values ranging from 0×10^{-15} to 40×10^{-15}) or natural Chilean samples (^{36}Cl/Cl values ranging from 22×10^{-15} to 590×10^{-15}) (Sturchio et al., 2009, 2011). Additional details on ^{36}Cl are provided in Section 3.3. However, the current data indicate that analysis of ^{36}Cl can provide important evidence concerning the origin of ClO_4^- in environmental samples. Therefore, the basic method for analysis is provided herein.

Analysis of ^{36}Cl in ClO_4^- is performed by AMS using Cl^- derived from ClO_4^-. There are a limited number of AMS facilities in the United States, and the ^{36}Cl analyses on ClO_4^- reported to date have been performed at the Purdue Rare Isotope Measurement Laboratory (PRIME) at Purdue University (www.physics.purdue.edu/primelab). The basic procedure used to produce Cl^- for AMS is as described in Section 2.5.2 of this document to the point of AgCl precipitation, washing, and drying of crystals (i.e., prior to the reaction with CH_3I). Generally, a portion of the sample prepared to this step for Cl stable isotopic analysis is saved for ^{36}Cl analysis. The AgCl is subsequently redissolved and the Cl^- is purified twice by anion chromatography (using a method developed by the PRIME Lab at Purdue University; http://www.physics.purdue.edu/primelab/AMSQAQC/chemProc004.pdf) to ensure removal of trace amounts of sulfure (S) that might cause isobaric interference at mass 36. Purified Cl^- is

then re-precipitated as AgCl for AMS measurement. Analysis of seawater Cl⁻ provides a reference datum of ^{36}Cl/Cl = 0.5 × 10⁻(Argento et al., 2010).

2.7 SUMMARY OF SAMPLING, PURIFICATION, AND ANALYSIS OF CHLORINE AND OXYGEN ISOTOPES IN PERCHLORATE

A summary of the general procedures involved in the collection, purification, and analysis of ClO_4^- samples for Cl and O isotopes is provided in Figure 2.10. The procedures, which are provided in detail in the previous sections, are summarized as follows:

1. ClO_4^- (10 mg) is collected directly from groundwater using IX resin columns or collected from mineral deposits or soils by extraction of solids with ClO_4^--free water and collection of dissolved ClO_4^- from the extract using IX resin columns. Columns can be preserved with 0.05 N HCl.

2. The ClO_4^- is then eluted from the IX column after an initial wash with 4 M HCl to remove impurities using a solution with $FeCl_4^-$. Fractions are collected during the elution phase to minimize total volume of the ClO_4^- -bearing eluent.

3. The ClO_4^- in the eluent subsequently is purified by a series of steps that include Fe removal by either cation exchange or precipitation, and then the ClO_4^- is concentrated and unwanted salts are removed by precipitation and filtration. The dissolved ClO_4^- is then crystallized as $CsClO_4$, $KClO_4$, or $RbClO_4$.

4. The crystals are collected via filtration or evaporation and washed with methanol, after which the purity is determined by crystal morphology, Raman spectroscopy, or ion chromatography. If oxygen-containing impurities are detected at concentrations greater than 1% for the mole fraction of O in the ClO_4^- sample, the sample is repurified.

5. After crystals are determined to be pure, $\delta^{18}O$ is measured by on-line conversion to CO with CF-IRMS and $\delta^{18}O$ and $\Delta^{17}O$ are measured by off-line conversion to O_2 with DI-IRMS.

6. Aliquots of alkali halide (CsCl, RbCl, or KCl) remaining after the decomposition of ClO_4^- salts for O isotopic analyses (Step 5) are collected, converted to CH_3Cl, and then analyzed for $\delta^{37}Cl$ using either DI-IRMS or CF-IRMS, depending on sample size.

7. Additional aliquots of alkali halide from Step 5 are converted to AgCl and analyzed for ^{36}Cl/Cl by AMS.

Figure 2.10. Overview of the procedures involved in the collection, purification, and analysis of ClO_4^- samples for Cl and O isotopic composition.
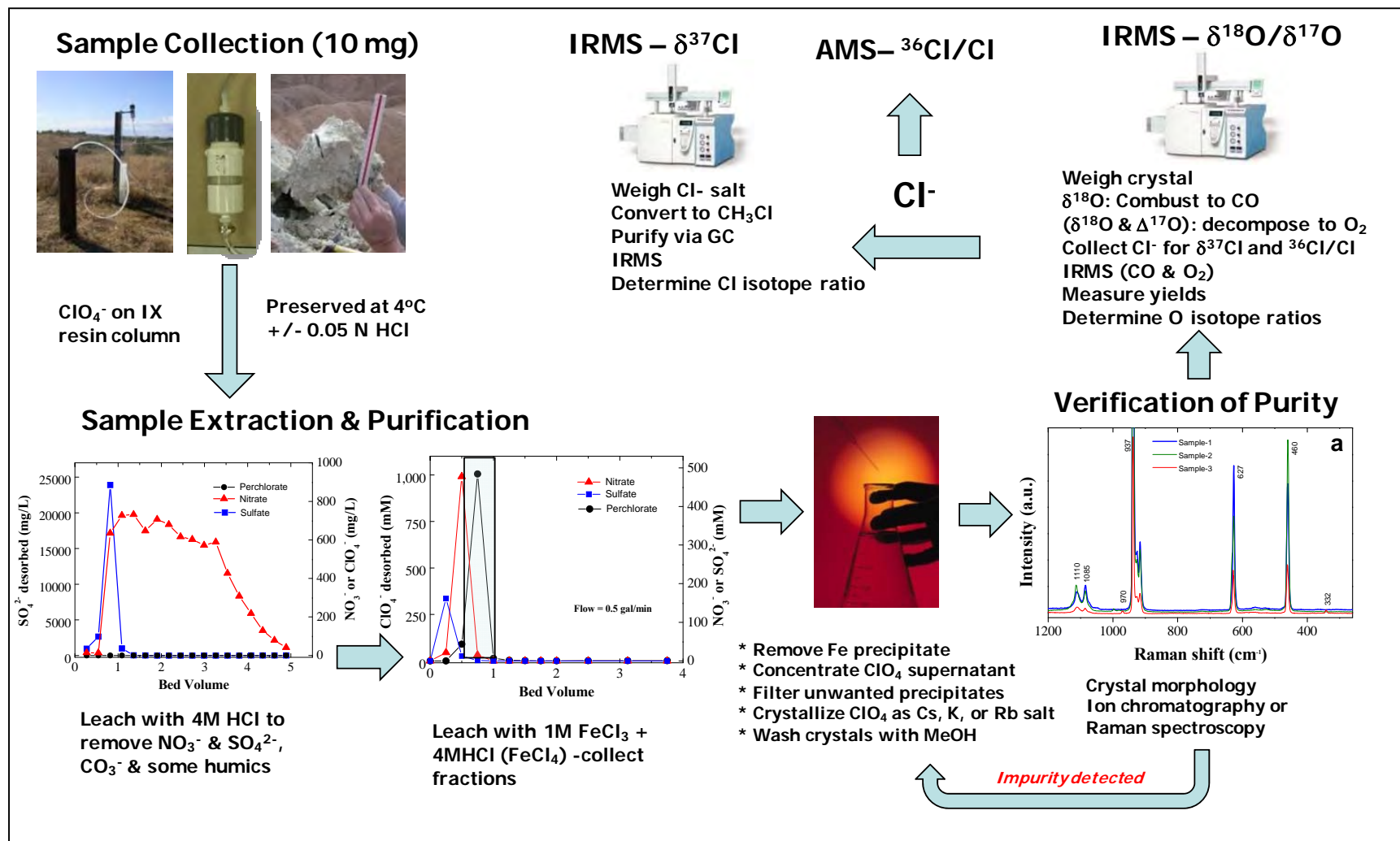
2.8 SUPPORTING INFORMATION FOR PERCHLORATE FORENSIC STUDIES

There are a variety of analytical techniques that can potentially provide important supporting information concerning the origin of ClO_4^- in groundwater (e.g., Clark and Fritz, 1997; Cook and Herczeg, 2000). Examples of relevant methods and basic sample collection procedures are provided in Table 2.1. Numerous laboratories conduct various combinations of these different types of analyses, including facilities at USGS, national laboratories, and universities. The supporting methods are described briefly in the sections below.

2.8.1 Field Parameters

Typical geochemical parameters should be collected at each well during ClO_4^- sampling using a field meter (e.g., YSI 6000 XL multiparameter meter; YSI Inc., Yellow Springs, OH). The parameters, which provide a basic geochemical baseline for each well, include temperature, dissolved oxygen, oxidation-reduction potential, conductivity, and pH. The stabilization of these parameters with time is used in low-flow sampling applications to determine when to collect field samples, as described in Section 2.2.2 of this document. In addition, these parameters can be useful for assessing relations between water masses and geochemical conditions that could affect the stability of ClO_4^- through biodegradation.

2.8.2 Groundwater-Age Dating

The age of groundwater (time since infiltration or recharge) is an important forensic tool for ClO_4^- that may be either natural or anthropogenic in origin, particularly given that much of the known synthetic ClO_4^- contamination in the U.S. occurred after the 1940s. Measurable groundwater ages in aquifers commonly range from years to millennia and therefore can be used to relate ClO_4^- occurrences to land-use history, as was recently done in Long Island, NY, in support of isotopic data showing that Chilean nitrate fertilizers account for some of the groundwater ClO_4^- in this region (see Section 4.0 and Böhlke et al., 2009). Groundwater ages between about 0 and 60 yr can be determined by analyses of atmospheric environmental tracers including tritium (^3H), sulfur hexafluoride (SF_6), and chlorofluorocarbons (CFCs), all of which have been incorporated in groundwater in varying concentrations since the middle of the 20th century (similar to synthetic ClO_4^-). Analyses of ^3He, the decay product of ^3H, provide additional estimates of groundwater age. Analysis of dissolved neon (Ne) also is conducted during tritium-helium age dating to evaluate degassing or the presence of excess air in samples. Groundwater ages on the order of 10^3 to 10^4 yr can be estimated from concentrations of ^{14}C, as was done in the southwestern United States to document the occurrence of natural (pre-anthropogenic) ClO_4^- (Plummer et al., 2006; Jackson et al., 2010). Descriptions of collection and interpretation of groundwater-age data are described in several publications (Cook and Herczeg, 2000; Busenberg and Plummer, 1992, 2000), with additional details in the following sources and references therein (Thatcher et al., 1976; USGS, 2011a).

2.8.3 Stable Hydrogen and Oxygen Isotopes in Water

The stable H and O isotopic composition of H_2O is used commonly to distinguish sources of water, effects of evaporation, and in some cases relative ages of groundwater (Coplen et al., 2000; Clark and Fritz, 1997), all of which may be useful in some situations for distinguishing sources of ClO_4^-. Analyses of H and O isotopes in water can be performed

by equilibration with H_2 and CO_2, respectively, for mass spectrometry (Coplen et al., 1991; Révész and Coplen, 2011; USGS, 2011b).

2.8.4 Stable Nitrogen and Oxygen Isotopes in Nitrate

Nitrate (NO_3^-) commonly occurs with ClO_4^- because both are produced naturally in the atmosphere, both may be introduced by agricultural practices, and both have similar transport properties and similar susceptibility to biodegradation. Therefore, stable isotopic and other evidence for the origin and fate of NO_3^- (Heaton, 1986; Kendall and Aravena, 2000; Böhlke et al., 2002; Böhlke et al., 1997; Michalski et al., 2004; McMahon and Böhlke, 2006) can provide important information concerning the origin and behavior of coexisting ClO_4^- in some situations (e.g., Plummer et al., 2006; Jackson et al., 2010). The stable isotopes of N and O in NO_3^- can be analyzed by various methods, including bacterial conversion to nitrous oxide (N_2O) and continuous-flow mass spectrometry (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004; Révész and Coplen, 2011; USGS, 2011b).

2.8.5 Stable Sulfur and Oxygen Isotopes in Sulfate

Sulfate (SO_4^{2-}) is another oxyanion that may be associated with ClO_4^- as a result of atmospheric deposition or anthropogenic applications, and it may indicate changes in redox conditions that affect ClO_4^- transport. Stable isotopic analyses of SO_4^{2-} can be useful in evaluating sources and fate of SO_4^{2-} (Krouse and Grinenko, 1991; Krouse and Mayer, 2000), which may provide information about ClO_4^- distribution in aquifers. The stable isotopes of sulfur (S) and oxygen in SO_4^{2-} can be analyzed by high-temperature conversion of $BaSO_4$ to sulfur dioxide (SO_2) and CO, respectively, for mass spectrometry (Carmody et al., 1998; Révész and Coplen, 2011; USGS, 2011b).

2.8.6 Dissolved Gas Concentrations

Concentrations of dissolved gases provide important information about groundwater recharge temperatures (Ar, N_2, Ne krypton [Kr], xenon [Xe]) and subsurface redox reactions (O_2, methane [CH_4], N_2). Recharge temperatures are important for the estimation of groundwater ages from atmospheric environmental tracers (Section 2.8.2) and they may be useful for distinguishing water masses from different sources and ages (Cook and Herczeg, 2000). In addition, past and current redox conditions are critical for understanding the potential for ClO_4^- biodegradation in aquifers (e.g., Coates and Achenbach, 2004). Dissolved N_2 concentrations can be used to assess whether a sample has experienced denitrification (e.g., Böhlke et al., 2002), which typically precedes ClO_4^- reduction as conditions become reducing. Major dissolved gases can be analyzed by gas chromatography on equilibrated headspace (USGS, 2011a). Neon analyses typically are done as part of the [3]H-[3]He groundwater dating method (USGS, 2011a).

2.8.7 Trace Element Concentrations

Trace element analysis may be helpful, for example where fireworks are a potential source of ClO_4^-. Elements commonly associated with fireworks include aluminum (Al), antimony (Sb), barium (Ba), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), and strontium (Sr), (Conklin, 1985) and correlations between ClO_4^- and these elements are possible if fireworks are a source (e.g., Böhlke et al., 2009). A common method for

analysis of trace elements is inductively coupled plasma mass spectrometry (ICP-MS), according to modified USEPA Method 200.8 (USEPA, 1994).

2.8.8 Anion Concentrations

Typical groundwater anions, including NO_3^-, Cl^-, bromide (Br^-), and SO_4^{2-} can be measured, in addition to ClO_4^-, to provide geochemical background information for each well. It may also be useful to measure iodate (IO_3^-), which can form atmospherically and has been observed to co-occur with natural ClO_4^- in groundwater beneath the Southern High Plains (SHP) of West Texas and New Mexico (Dasgupta et al., 2005). Samples should be filtered (preferably with pore size 0.2 µm or smaller) in the field to minimize the possibility of biodegradation of some anions during storage. The anions, except IO_3^-, can be analyzed by ion chromatography according to USEPA Method 300.0. IO_3^- can be measured using high performance liquid chromatography with ultraviolet detection (HPLC-UV), as described in Dasgupta et al. (2005) or by liquid chromatography−tandem mass spectrometry (LC−MS/MS) (Snyder et al., 2005).

Table 2.1 Examples of supporting analytical methods and sampling requirements.

Field Measurement		Equipment			
Temperature		Field meter			
Specific conductivity		Field meter			
pH		Field meter			
Dissolved O_2		Field meter			
Reduction potential		Field meter			
Sample	**#**	**Container**	**Filter**	**Treatment**	**Analytical Lab**
Water H and O isotopes*	2	60-mL glass, Polyseal cap	no	small headspace, ship cool	USGS
Tritium* (groundwater dating)	2	500-mL glass, Polyseal cap	no	small headspace, ship cool	USGS
Major gases*	3	serum bottle, pre-weighed butyl stopper, crimper-top	no	no bubbles, 1 KOH pellet, cap underwater, 4 °C	USGS
He and Ne isotopes* (groundwater dating)	3	Copper (Cu) tube, crimped	no	no bubbles, backpressure, crimp while flowing	USGS
CFC* Groundwater dating)	5	CFC bottle, Al-lined cap	no	no bubbles, cap underwater, tape on cap, 4 °C	USGS
SF_6* (groundwater dating)	2	2.5-L glass, Polyseal cap	no	no bubbles	USGS
Trace elements	2	125-mL HDPE, acid-rinsed	0.2 µm	In-line filter, 1 mL clean HNO_3	USGS
Anions	2	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Shaw Environmental
NO_3^- N and O isotopes	1	1-L high density polyethylene (HDPE), Polyseal cap	0.2 µm	KOH pellets (pH>11)	USGS
SO_4^{2-} S and O isotopes (>20 mg/L)*	1	- L HDPE, Polyseal cap	0.2 µm	None – ship cool	USGS
SO_4^{2-} S and O isotopes (<20 mg/L)*	1	resin cartridge, HCl, barium chloride ($BaCl_2$), bucket	in cartridge	None – ship cool	USGS
Perchlorate (ClO_4^-)	1	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Shaw Environmental
Iodate (IO_3^-)	1	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Texas Tech University

Methods and laboratories commonly used for field studies conducted for ESTCP-ER200509; other procedures and laboratories are also available.

* For additional details, see the following websites: http://isotopes.usgs.gov/; http://water.usgs.gov/lab/cfc/.

3.0 RESULTS AND INTERPRETATIONS

This section of the document (1) summarizes the stable Cl and O isotope characteristics of synthetic and natural ClO_4^- in "source" samples (e.g., Chilean fertilizer, commercial reagents, fireworks, flares, etc.); (2) describes potential isotopic effects of post depositional processes such as biodegradation and O exchange of ClO_4^-, and (3) provides examples of recent forensic evaluations of ClO_4^- in groundwater at different sites. Section 4.0 provides a recent case study of Cl and O isotopic analyses conducted on Long Island, NY, to distinguish ClO_4^- sources.

3.1 STABLE ISOTOPES OF CHLORINE AND OXYGEN IN SYNTHETIC PERCHLORATE

Synthetic ClO_4^- is synthesized electrochemically using NaCl and H_2O (Schumacher, 1960). Samples from a variety of different synthetic sources, including laboratory reagents, commercial manufacturers, and ClO_4^- derived from road flares, fireworks, Pyrodex gunpowder, and chlorate herbicides, have been analyzed for Cl and O stable isotopes. Additional details on these samples are provided in Bao and Gu (2004), Böhlke et al. (2005), and Sturchio et al. (2006, 2011). Some data are unpublished results from ESTCP Project ER-200509. Data for samples of synthetic ClO_4^- in which both $\delta^{18}O$ and $\delta^{37}Cl$ values were measured are shown in Figure 3.1, and specific samples grouped by manufacturer (source) are shown in Figure 3.2. In addition, the complete published dataset is provided in Appendix A.

The $\delta^{37}Cl$ values of all synthetic ClO_4^- samples presented in Figure 3.1 group within a range from -3.1‰ to +2.3‰ and have a mean value of ~+0.6‰. This value is near that reported for common industrial sources of NaCl, such as halite from Phanerozoic bedded evaporates, which has reported $\delta^{37}Cl$ values of 0.0±0.9 ‰ (Eastoe et al., 2007). The electrochemical synthesis of ClO_4^- is nearly stoichiometric for Cl^- (i.e., nearly all of the added Cl^- is converted to ClO_4^-), so it is not surprising that the Cl isotope values in the resulting ClO_4^- are similar to those in the starting NaCl. The current $\delta^{18}O$ values of synthetic ClO_4^- vary over a wider range than for $\delta^{37}Cl$, from -24.8‰ to -12.5‰ (Figure 3.1). It has been hypothesized that the $\delta^{18}O$ values of the synthetic ClO_4^- samples reflect the $\delta^{18}O$ in the H_2O used for production, and that some O isotopic fractionation occurs during ClO_4^- synthesis (Sturchio et al., 2006). In one set of samples in which $\delta^{18}O$ was measured in both the produced ClO_4^- and the local meteoric H_2O used in the synthesis, the observed difference was ~7‰ (Sturchio et al., 2006). In contrast to $\delta^{18}O$, $\Delta^{17}O$ values of all synthetic ClO_4^- samples analyzed to date are 0.0±0.1 ‰ (when calibrated by assuming USGS37 reference material has $\Delta^{17}O=0$), indicating that there is negligible mass-independent isotopic fractionation of O during ClO_4^- synthesis (Sturchio et al., 2006, 2011).

When multiple samples of ClO_4^- from individual manufacturers have been analyzed, the $\delta^{18}O$ and $\delta^{37}Cl$ values group closely together (Figure 3.2). For example, the $\delta^{18}O$ values of three salts produced by Manufacturer A ($KClO_4^-$, $NaClO_4^-$, and $NH_4ClO_4^-$, respectively) ranged from -21.3 to -22.3 ‰ (-21.7±0.5‰) and the $\delta^{37}Cl$ value for all three samples was +0.4‰ (from Sturchio et al., 2006). The $\delta^{18}O$ for ClO_4^- salts from Manufacturer B ranged from -15.6 to -16.3 ‰ (-16.1±0.5 ‰) and the $\delta^{37}Cl$ values averaged +0.8±0.6 ‰. In this specific instance, the $\delta^{18}O$ values of ClO_4^- produced by the two manufacturers would permit the two sources to be distinguished (i.e., the values between manufacturers are statistically different). However, use of stable isotopes to distinguish synthetic sources of ClO_4^- in the field may be limited by

uncertainties about undocumented sources. Substantial isotopic differences among synthetic ClO_4^- sources mainly occur in $\delta^{18}O$ and, in contrast to the specific example provided in Figure 3.2, there is substantial overlap in the $\delta^{18}O$ values of different products tested to date, as is apparent from the data in Figure 3.1. In addition, differences in $\delta^{18}O$ values for ClO_4^- produced by a single manufacturer in different batches or over long time periods have not been studied.

In addition to electrochemical synthesis, ClO_4^- is known to be produced over time (to concentrations of the order of milligrams per liter) in hypochlorite solutions (e.g., commercial bleach) by disproportionation reactions (Kang et al., 2006; Trumpolt et al., 2005). Only two samples of ClO_4^- derived from bleach have thus far been analyzed, and both samples had unusually low values of $\delta^{18}O$ (<-50‰) and high values of $\delta^{37}Cl$ (>+9‰) (ESTCP Project ER-200509, unpublished data). If similar values are found as more samples are analyzed, $\delta^{18}O$ and $\delta^{37}Cl$ values may be useful for distinguishing ClO_4^- derived from bleach from that produced by electrochemical synthesis.

Figure 3.1. Values of $\delta^{37}Cl$ versus $\delta^{18}O$ for samples of synthetic ClO_4^- from different sources. Analytical uncertainty is ~±0.3‰. Dashed line is $\delta^{37}Cl$ reference value of 0 for SMOC.

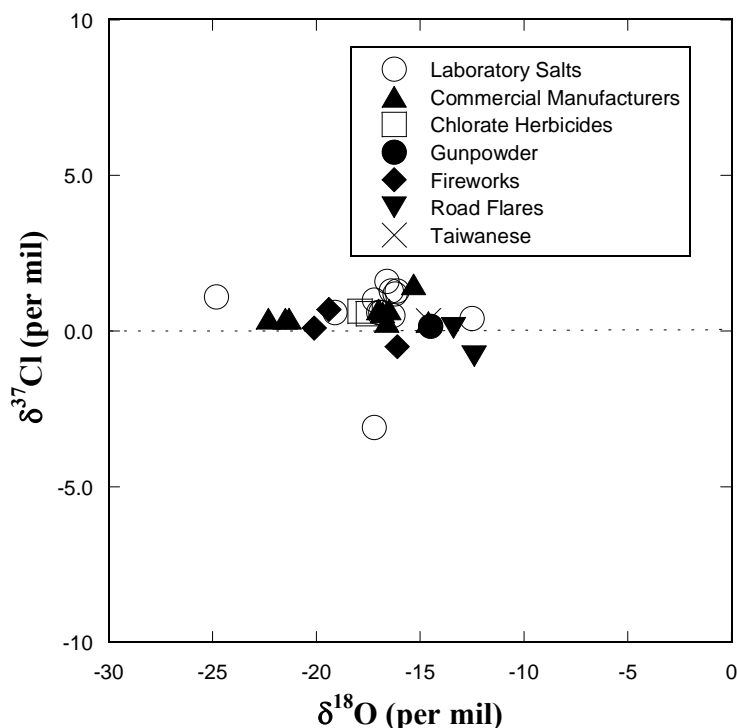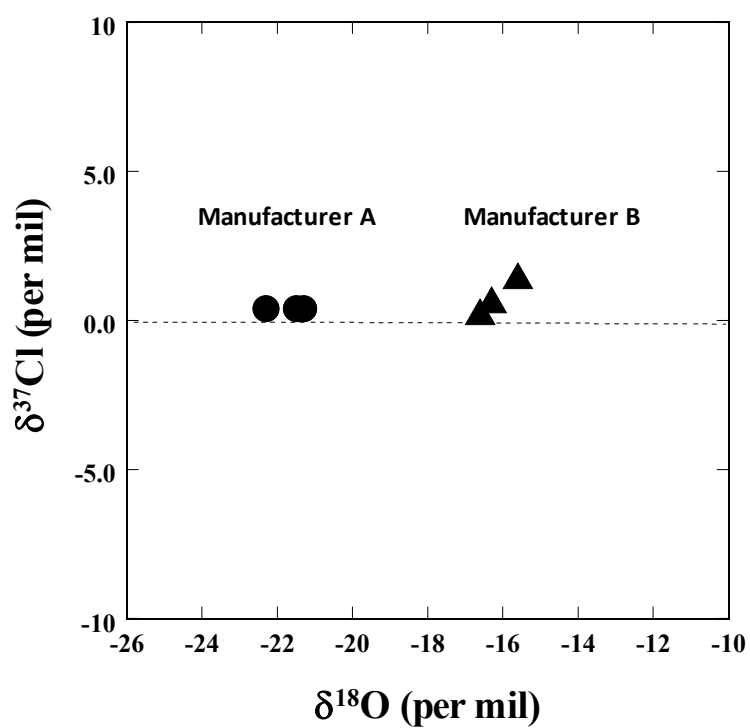**Figure 3.2. Values of $\delta^{37}Cl$ versus $\delta^{18}O$ for samples of synthetic ClO_4^- from two different manufacturers.** Analytical uncertainty is ~±0.3‰. Dashed line is $\delta^{37}Cl$ reference value of 0 for SMOC.

3.2 STABLE ISOTOPES OF CHLORINE AND OXYGEN IN NATURAL PERCHLORATE

3.2.1 Chilean Nitrate Deposits and Imported Fertilizer

As described in Section 1.1.2, the most well-known source of natural ClO_4^- is nitrate deposits from the Atacama Desert of Chile (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2005). These nitrate deposits, which are also called "Chilean caliche," were widely imported into the United States during the 20th century as a source of inorganic nitrogen fertilizer. It is estimated that ClO_4^- derived from Chilean fertilizers represents an equivalent source to that of synthetic products in terms of ClO_4^- exposure risk through incorporation of ClO_4^- into the food chain (Dasgupta et al., 2005).

Values of $\delta^{18}O$ and $\Delta^{17}O$ in ClO_4^- from the Atacama Desert were first reported by Bao and Gu (2004). The $\delta^{18}O$ values in the Chilean samples that they analyzed (three caliche samples and one sample of imported fertilizer) ranged from -24.8‰ to -4.5‰ and $\Delta^{17}O$ values ranged from +4.2‰ to +9.6‰, with an average value of +8.0‰. The original observation that Chilean ClO_4^- has substantial ^{17}O excess (i.e., ^{17}O higher than that expected from mass-dependent isotopic fractionation, which should yield $\Delta^{17}O$ near 0), was subsequently confirmed by analysis of a large number of additional ClO_4^- samples from Atacama Desert caliche deposits, groundwater, and imported Chilean fertilizers from this region (Böhlke et al., 2005; Sturchio et al., 2006, 2011; Jackson et al., 2010) (Figure 3.3). These studies also documented that the $\delta^{37}Cl$ values of the Chilean materials are significantly lower than those of synthetic ClO_4^-, ranging from -14.5‰ to -11.8‰.

The high values of $\Delta^{17}O$ in the Chilean samples are interpreted to indicate an atmospheric origin of this natural ClO_4^- by photochemical reactions between volatile Cl species and ozone (O_3), the latter of which is also known to be characterized by large positive $\Delta^{17}O$ values (Johnson et al., 2000; Bao and Gu, 2004). The formation of ClO_4^- with O_3 as a reactant was also recently confirmed in laboratory studies (Kang et al., 2008; Rao et al., 2010), and subsequent isotopic analysis of the O_3-generated ClO_4^- revealed a large positive $\Delta^{17}O$ value (Rao et al., unpublished data), further supporting the theory of atmospheric formation of natural ClO_4^- via O_3.

Dual isotope plots comparing $\delta^{37}Cl$ versus $\delta^{18}O$ and $\Delta^{17}O$ versus $\delta^{18}O$ in natural and synthetic ClO_4^- are provided in Figure 3.4. The plots are composed of data collected to date from the published literature (Sturchio et al., 2006, 2011; Böhlke et al., 2009; Jackson et al., 2010). These isotope data are also provided in Appendix A. The mean values for Chilean ClO_4^- for $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ are -12.6±1.5‰ (n=13), -6.6±2.1‰ (n=17) and +9.2±0.7‰ (n=17), respectively. One anomalous value from Bao and Gu, (2004), labeled with an asterisk in Plot B, is excluded from the above averages, but additional samples have been collected from different regions of the Atacama Desert to provide a more reliable determination of the range in $\Delta^{17}O$. The isotope data from these samples are not yet available (ESTCP Project ER-200509).

As shown in the dual isotope plots in Fig 3.4, there are consistent and significant isotopic differences between natural Chilean ClO_4^- and synthetic ClO_4^-. Most significantly, the high $\Delta^{17}O$ values for the Chilean materials (average of +9.2‰) clearly differentiate this ClO_4^- source from all synthetic sources, for which the average value $\Delta^{17}O$ value is near 0, consistent with typical

mass-dependent isotopic fractionation of ^{16}O, ^{17}O, and ^{18}O (Fig 3.4, Plot A). The low $\delta^{37}Cl$ values (average of -12.6‰) also clearly distinguish Chilean ClO_4^- from all synthetic sources, which have an average $\delta^{37}Cl$ value of +0.8‰. Thus, both $\Delta^{17}O$ and $\delta^{37}Cl$ can be used to differentiate these two sources in forensic studies.

3.2.2 Indigenous Sources in the Southwestern United States

As previously discussed in Section 1.1.3, research conducted during the past decade has revealed that natural ClO_4^- occurs in arid environments other than the Atacama Desert of Chile. Most significantly for forensic studies in the United States, indigenous natural ClO_4^- has been widely detected in the southwestern United States, as evidenced through various surveys of ClO_4^- in surface soils, vadose-zone profiles, wet and dry deposition, and groundwater in New Mexico, Texas, California, and elsewhere in this region (Dasgupta et al., 2006; Plummer et al., 2006; Rajagopalan et al. 2006, 2009; Rao et al., 2007; Parker et al., 2008; Jackson et al., 2010). Recent detections of ClO_4^- in Antarctic soils and on Mars have caused additional interest in the mechanisms of formation and accumulation of natural ClO_4^- (Hecht et al., 2009; Ming et al., 2010; Catling et al., 2010; Kounaves et al., 2010).

The stable isotopic composition of indigenous natural ClO_4^- from several locations and environments (vadose zone, caliche deposits, groundwater) in the southwestern United States was reported recently by Jackson et al. (2010). One group of groundwater samples was collected from a large area of the Southern High Plains (SHP) of West Texas and New Mexico (n=8), and the Middle Rio Grande Basin (n=2) (grouped together with Southern High Plains in Figure 3.4). One soil sample from West Texas was also analyzed. All of these indigenous samples are similar isotopically, despite the large areal extent over which they were collected, with $\delta^{37}Cl$ values ranging from +3.1 to +5.0‰, $\delta^{18}O$ values ranging from +0.6 to +3.8‰, and $\Delta^{17}O$ values ranging from +0.3 to +1.3‰. The data indicate that ClO_4^- from the SHP region of Texas and New Mexico is consistently different from both Chilean ClO_4^- and synthetic ClO_4^- when all relevant stable isotopic abundances are considered (^{16}O, ^{17}O, ^{18}O, ^{35}Cl and ^{37}Cl) (Figure 3.4). The small, but significantly positive $\Delta^{17}O$ values of these samples indicate that either (1) they were formed predominantly by a different mechanism than the Chilean ClO_4^-, which has much higher average $\Delta^{17}O$ (hypothesized to originate from O_3 as a reactant) or (2) the ClO_4^- was affected by post depositional O exchange (see Section 3.3 for additional information on post depositional reactions).

A second group of ClO_4^- samples (n=4) represented in Fig 3.4 was collected from NO_3^-- rich caliche deposits around the southern end of Death Valley, CA, within the Mojave Desert (see map in Jackson et al., 2010). These deposits, which have ClO_4^- concentrations ranging from 0.25 to 1.7 mg/kg (about one to three orders of magnitude lower than the Atacama deposits) are characterized by ClO_4^- with an isotopic signature that is distinctive from the Chilean and synthetic ClO_4^-, and from those from the SHP. In comparison to the SHP samples, the Death Valley samples have lower $\delta^{37}Cl$ values (from -0.8 to -3.7‰) and much higher $\Delta^{17}O$ values (+8.6 to +18.4‰). As is apparent from Figure 3.4, Plot B, the $\Delta^{17}O$ values of the Death Valley samples are similar to or, in some instances, higher than those of the Chilean samples, indicating an important component of atmospheric origin and relative lack of post depositional exchange of O with terrestrial materials. The SHP and Death Valley samples can be considered together as U.S. indigenous sources and, even though there are substantial ranges in the individual isotope

values, this indigenous grouping remains isotopically distinct from synthetic and Chilean ClO_4^- when all relevant isotopes are considered.

Figure 3.3. Values of $\Delta^{17}O$ versus $\delta^{18}O$ in Chilean and synthetic C lO$_4^-$. The single value with an asterisk is from Bao and Gu (2004).
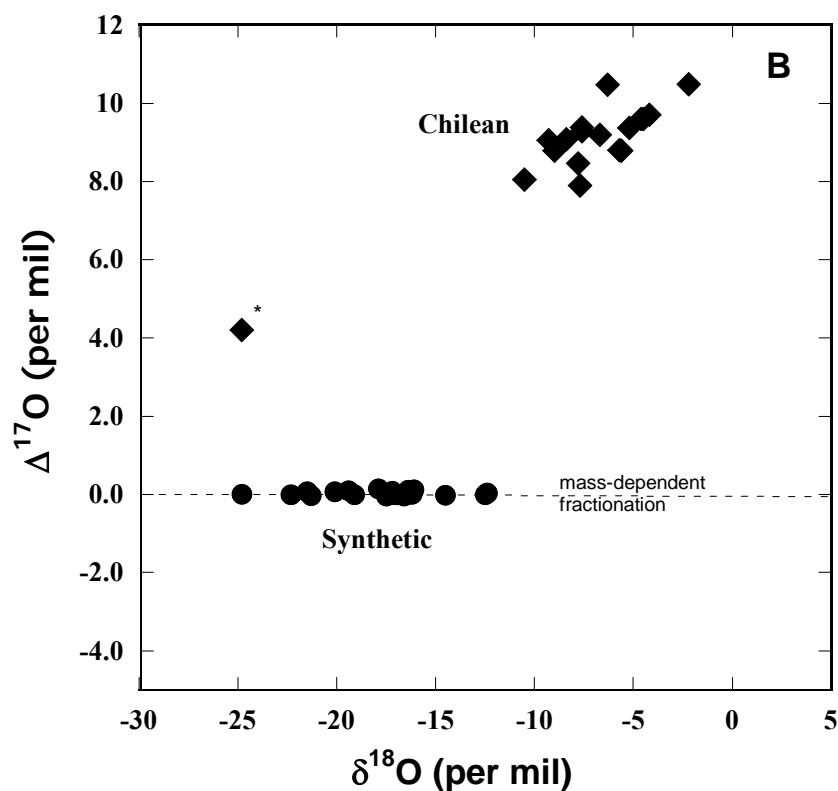
Figure 3.4. Comparison of $\delta^{37}Cl$ versus $\delta^{18}O$ (Plot A) and $\Delta^{17}O$ versus $\delta^{18}O$ (Plot B) in natural indigenous ClO_4^- in the United Stat es, natural Chilean ClO_4^-, and synthetic ClO_4^-. The single value on Plot B labeled with an asterisk from Bao and Gu (2004) is distinct from all other results from Chilean samples reported to date.
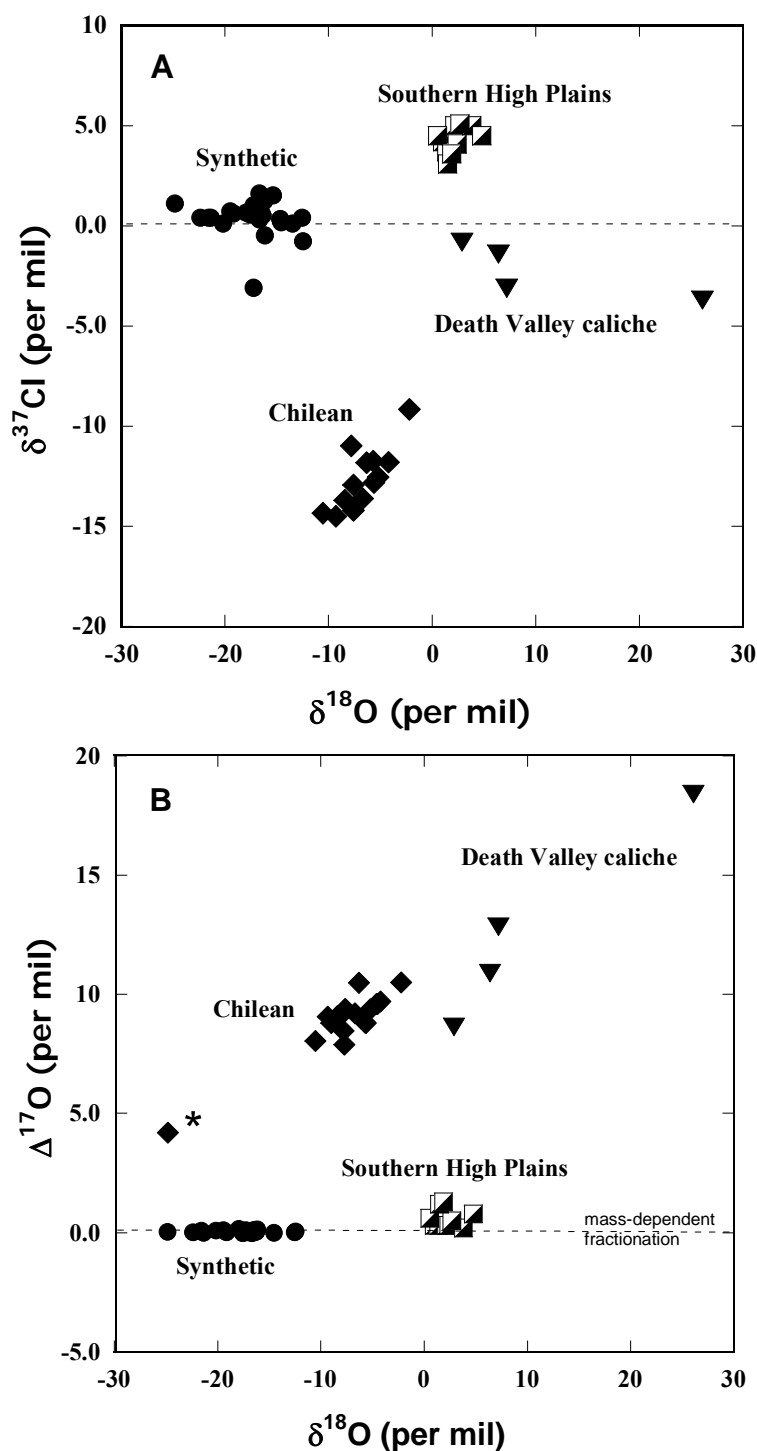
3.3 ABUNDANCE OF ^{36}Cl IN SYNTHETIC AND NATURAL PERCHLORATE

The abundance of the radioactive isotope ^{36}Cl (reported as atom fraction, or mole fraction, designated traditionally as ^{36}Cl/Cl) has proven to be another important tool for distinguishing ClO_4^- sources (see Section 2.6 for additional background). Chlorine-36 is present naturally in Cl^- in groundwater in the United States, with ^{36}Cl/Cl values ranging from ~10×10^{-15} near coasts to as high as ~1700×10^{-15} in the central Rocky Mountains (Bentley et al., 1986; Phillips, 2000; Davis et al., 2003). Until recently, values of ^{36}Cl/Cl in ClO_4^- were unknown. However, Sturchio et al. (2009) reported values of ^{36}Cl/Cl in 35 different ClO_4^- samples from synthetic, Chilean, and Southwestern U.S. sources ranging over more than four orders of magnitude (Figure 3.5). Synthetic ClO_4^- samples were characterized by relatively low values of ^{36}Cl/Cl from 0×10^{-15} to 40×10^{-15} (Sturchio et al., 2009). These values are consistent with Cl sources such as the geologically ancient halite-rich evaporate deposits (e.g., salt domes, bedded salts) from which large amounts of NaCl are mined commercially in the form of rock salt.

In contrast to synthetic samples, all indigenous natural ClO_4^- samples from the southwest United States that were tested (including some of the SHP groundwater samples and Death Valley deposits described in Section 3.2.2 and shown in Figure 3.4 with differing δ^{37}Cl and Δ^{17}O) had unusually high ^{36}Cl/Cl values, ranging from 3130×10^{-15} to $28,800 \times 10^{-15}$. The presence of bomb-generated ^{36}Cl from nuclear tests in the mid 1950s (Phillips, 2000; Davis et al., 2003) could not be ruled out for a few of the samples, but ^{36}Cl/Cl values as high as $12,300 \times 10^{-15}$ were measured in ClO_4^- from groundwater in New Mexico with recharge ages estimated at >5000 yr (Plummer et al., 2006; Sturchio et al., 2009). High concentrations of ^{36}Cl in some ClO_4^- samples may point toward the stratosphere, rather than the troposphere, as an important area of atmospheric ClO_4^- formation (Sturchio et al., 2009). Natural ClO_4^- from Chilean deposits had ^{36}Cl/Cl values from 22×10^{-15} to 590×10^{-15}, much lower than any of the natural samples from the southwest United States. The Chilean samples originally may have had high ^{36}Cl/Cl values resulting from stratospheric production, but may have lost much of that activity via radioactive decay. This could be consistent with a relatively long history of Atacama ClO_4^- accumulation, as hyper-arid conditions in this region may have persisted for at least 3 to 8 million years (Myr) (Alpers and Brimhall, 1988; Hartley and Chong, 2002), which is 10 or more times the half-life of ^{36}Cl. Values of ^{36}Cl/Cl in Cl^- from the Atacama Desert are similar to those of the associated ClO_4^-, as shown in Figure 3.5. The accumulation time of ClO_4^- in the arid southwest United States appears to have been much shorter (of the order of 10^4 yr), and natural ClO_4^- accumulated from the atmosphere during this time would be expected to possess most of its original ^{36}Cl activity (Jackson et al., 2010). Most importantly for forensic studies of ClO_4^-, in combination with stable isotope ratios of O and Cl, ^{36}Cl abundances can provide important supporting data to help differentiate synthetic, Chilean, and indigenous U.S. sources.

Figure 3.5. Values of ^{36}**Cl/Cl (mol e fracti on) versus** δ^{37}**Cl in repr esentative s amples o f synthetic ClO**$_4^-$ **reagents and products, natural ClO**$_4^-$ **extracted from soil and groundw ater from the Atacama Desert , Chile, and natural ClO**$_4^-$ **extracted from groundw ater and soil from the southwestern United States** (modified from Sturchio et al., 2009)**.**
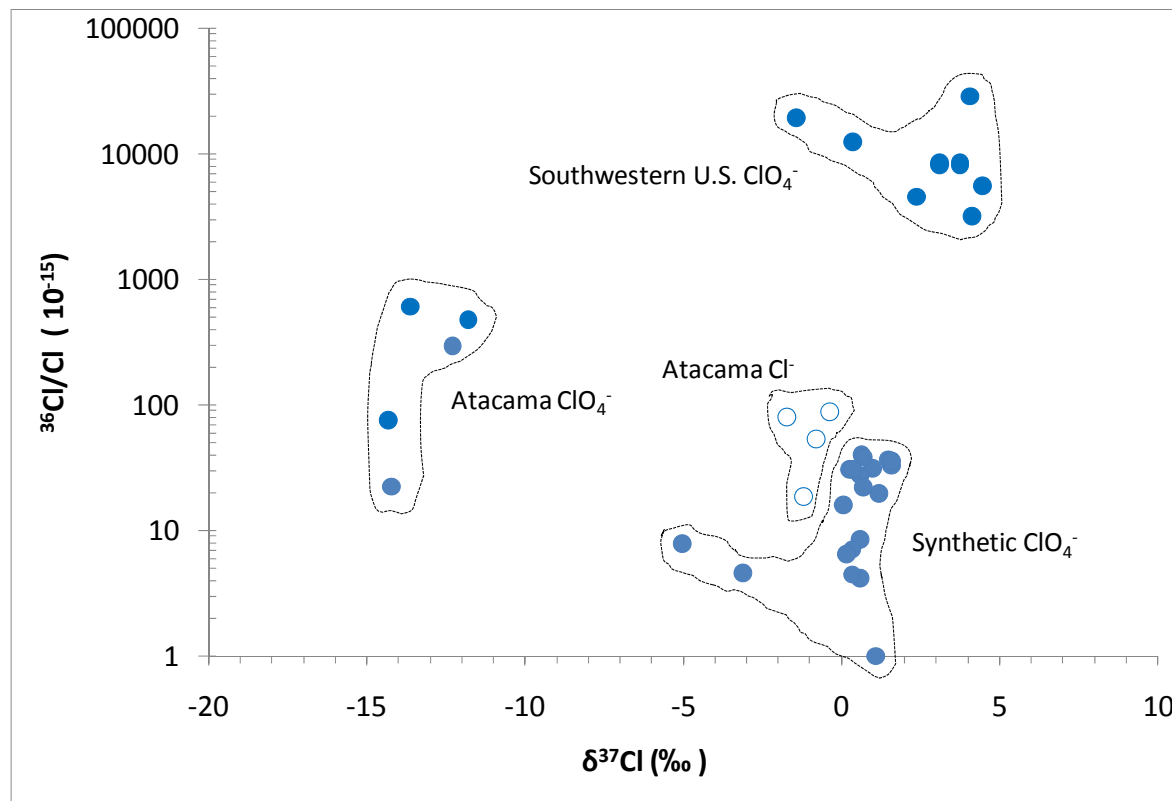
3.4 POST DEPOSITIONAL MODIFICATION OF CHLORINE AND OXYGEN ISOTOPES IN PERCHLORATE

One important premise of a forensic investigation involving stable isotopes is that either (1) the stable isotope signatures in a molecule are preserved after deposition (by either natural mechanisms or contamination with synthetic sources) or (2) if they are not preserved, they are modified by known processes in a predictable fashion. One of the processes that is well known to alter the stable isotope composition of a molecule is biodegradation (e.g., Sharp, 2007; Hunkeler et al., 2008). In fact, systematic enrichments in the heavier isotopes of elements in reactive compounds (e.g., ^{13}C in methyl tert-butyl ether [MTBE], ^{15}N and ^{18}O in NO$_3^-$) have been used extensively to document biodegradation and to estimate kinetics of the process. Other processes, including isotopic exchange with surrounding compounds, can also alter isotope values in a compound of interest, and must be evaluated. The isotopic effects of biodegradation on both Cl and O in ClO$_4^-$ have been investigated in both laboratory and field experiments during the past few years (see Section 3.4.1), and studies are currently ongoing to evaluate the potential

isotopic effects of O exchange between ClO_4^- and other environmental components including H_2O (Section 3.4.2).

3.4.1 Isotopic Fractionation of Chlorine and Oxygen during Perchlorate Biodegradation

The fractionation of Cl and O stable isotopes through microbial reduction of ClO_4^- has been investigated in laboratory studies with pure cultures and in a field experiment involving a push-pull test (Coleman et al., 2003; Sturchio et al., 2003, Sturchio et al., 2007, Hatzinger et al., 2009). The equations used to describe isotopic fractionation of reactants are provided below (from Sturchio et al., 2007):

The isotopic fractionation factor, α, is defined as

[Eq. 3.1] $\alpha = R_A/R_B$

where R is an isotope ratio (Equation 3.1), and A and B are two compounds (product and reactant, respectively). For O and Cl isotope ratios, R represents $N(^{18}O)/N(^{16}O)$ or $N(^{37}Cl)/N(^{35}Cl)$, respectively, where N is number of entities (atoms). Values of α can be obtained from experimental data by assuming the exponential function:

[Eq. 3.2] $R/R_0 = f^{\alpha-1}$

where R and R_0 are the O or Cl isotope ratios of the residual ClO_4^- and the initial (unreacted) ClO_4^-, respectively, and f is the fraction of ClO_4^- remaining. The δ values of ClO_4^- are calculated using the following relationship:

[Eq. 3.3] $(\delta + 1)/(\delta_0 + 1) = f^{\alpha-1}$

where δ is the isotopic composition of the ClO_4^- at any value f, and δ_0 is the isotopic composition at $f=1$. The value of α can be calculated from the natural logarithm of Eq 3.2, as shown below:

[Eq. 3.4] $\alpha-1 = \ln (R/R_o)/\ln f$

The relation in Eq 3.4 describes the mass-dependent Rayleigh-type isotopic fractionation that accompanies a variety of natural processes (Clark and Fritz, 1997; Broecker and Oversby, 1971). Isotopic fractionation factors are commonly expressed in terms of ε, where

[Eq. 3.5] $\varepsilon = \alpha - 1,$

with ε typically reported in parts per thousand, or per mil (‰). Two independent studies evaluating the isotopic fractionation of Cl in ClO_4^- by the bacterial species A*zospira suillum* with acetate as the electron donor and ClO_4^- as the sole electron acceptor, reported $\varepsilon^{37}Cl$ values ranging from -12.9‰ to -16.6‰, depending on culture conditions (Coleman et al., 2003; Sturchio et al., 2003). Data for both Cl and O isotopic fractionation during microbial reduction of ClO_4^- were reported subsequently by Sturchio et al. (2007) using two bacterial genera (*Azospira* and *Dechlorospirillum*), each incubated at two different temperatures (22 °C and 10 °C, respectively). This study also evaluated the potential for O exchange during

biodegradation of ClO_4^- using ^{18}O-enriched H_2O. The $\varepsilon^{37}Cl$ values in the various experimental treatments varied from -14.5 to -11.5‰, and $\varepsilon^{18}O$ values ranged from -36.6 to -29.0‰. The ε values were independent of bacterial strain and temperature, and there was no evidence for O exchange between ClO_4^- and H_2O. One critical finding from this work was that the ratio of $\varepsilon^{18}O/\varepsilon^{37}Cl$ was nearly constant in all experiments (independent of strain or temperature or rate of reaction) at 2.50±0.04 over a range of f from 1.00 to 0.01 (Figure 3.6).

In a subsequent field study, water with ClO_4^- was injected into an aquifer that had previously been treated with soybean oil emulsion to stimulate ClO_4^- biodegradation, and then samples were collected over time from the injection well for analysis of stable isotopes and geochemical parameters (Hatzinger et al., 2009). The *in situ* isotopic fractionation factors ($\varepsilon^{37}Cl$ and $\varepsilon^{18}O$) from this study were 0.3-0.4 times the values previously reported for pure cultures, and the differences were attributed to physical and chemical heterogeneity in the aquifer. Similar effects have been observed during a number of other field studies of *in situ* isotopic fractionation, and modeling has illustrated how physical processes in heterogeneous hydrologic systems can cause field isotopic fractionation data to differ from lab data (Mariotti et al., 1988; Brandes and Devol, 1997; Green et al., 2010). Nonetheless, despite the differences in the magnitudes of the individual isotope effects, the $\varepsilon^{18}O/\varepsilon^{37}Cl$ ratio was 2.6, which is in excellent agreement with the laboratory-determined value of 2.5 as shown in Figure 3.6 and described further below (Sturchio et al., 2007). This indicates that the fundamental process by which ClO_4^- is reduced was the same in laboratory and field settings, but the heterogeneity of the field setting is such that it can lead to underestimation of the extent of ClO_4^- reduction when using an isotopic approach based solely on laboratory fractionation factors (Hatzinger et al., 2009).

The previous laboratory and field results concerning isotopic fractionation during biodegradation have implications for forensic studies. Isotopic analyses of O and Cl in ClO_4^- clearly show that different sources have distinct isotopic compositions, as described in Sections 3.1 and 3.2. However, variations in the isotopic composition of ClO_4^- in field samples could theoretically be caused by biodegradation or by mixing of isotopically distinct sources, and it is important to resolve these effects. Based on the laboratory and field studies conducted to date, biodegradation of ClO_4^- causes both $\delta^{18}O$ and $\delta^{37}Cl$ in the residual ClO_4^- (i.e., that remaining in the environment) to move along the slope shown in Figure 3.7. This trajectory (the slope of which is constant at $\varepsilon^{18}O/\varepsilon^{37}Cl=2.5$) is roughly perpendicular to the area in which mixtures of synthetic and Chilean ClO_4^- would plot. Thus, biodegradation will not obscure the difference between these two major sources. In Figure 3.7, the f values plotted on the upper sloping line indicate the calculated values of $\delta^{18}O$ and $\delta^{37}Cl$ in synthetic ClO_4^- when 10% (f=0.9), 20% (f=0.8), etc. are biodegraded, according to the lab data. Based on the field results of Hatzinger et al. (2009), the f values would remain much closer to the source material (i.e., at 30% biodegraded, the $\delta^{18}O$ and $\delta^{37}Cl$ values are predicted to be near f=0.9 on the curve in Figure 3.7). Different field settings might yield somewhat different degrees of scale contraction along this fractionation line. Most critically, however, the slope of the progression of $\varepsilon^{18}O/\varepsilon^{37}Cl$ is the same in the flask and field, such that synthetic and Chilean ClO_4^- will not overlap isotopically as a result of biodegradation.

The $\delta^{18}O$ and $\delta^{37}Cl$ values for ClO_4^- derived from the SHP place this material near the trajectory for a small subset of synthetic ClO_4^- samples as shown in Figure 3.8. The synthetic samples with the highest $\delta^{18}O$ values (i.e., ~-15‰) could overlap with SHP samples if they were extensively

biodegraded. Similarly, it is possible that $\delta^{18}O$ and $\delta^{37}Cl$ values for a Chilean ClO_4^- sample could become similar to those from Death Valley if the Chilean ClO_4^- were substantially biodegraded. However, it is important to note that $\Delta^{17}O$ values are almost unaffected by mass-dependent processes, so that large differences in $\Delta^{17}O$ between the sources would be preserved during degradation while $\delta^{18}O$ and $\delta^{37}Cl$ values were changing. Thus, from a practical perspective, potential "overlaps" in stable isotopic compositions caused by isotope effects of biodegradation are unlikely to cause mistakes in source delineation, particularly if ^{36}Cl analyses are conducted for samples and other supporting chemical and geochemical data are collected from sampling locations. For example, the potential for highly biodegraded (and isotopically fractionated) synthetic ClO_4^- to be confused for SHP natural ClO_4^- because of overlapping values of $\delta^{18}O$ and $\delta^{37}Cl$ can be further minimized by analyzing all samples in a forensic investigation for ^{36}Cl, as synthetic samples have low $^{36}Cl/Cl$ values (0×10^{-15} to 40×10^{-15}), whereas SHP and Death Valley samples have much higher $^{36}Cl/Cl$ values (3130×10^{-15} to $28,800 \times 10^{-15}$) (Sturchio et al., 2009), and these values should not be affected significantly by biodegradation. Similarly, Chilean and Death Valley samples analyzed to date have very different $^{36}Cl/Cl$ values.

In addition to ^{36}Cl, local geochemical parameters, including oxidation-reduction potential (ORP) and concentrations of dissolved oxygen (DO), dissolved organic carbon (DOC), NO_3^-, and N_2 (see Section 2.8) can provide important constraints on the potential for biodegradation. Bacteria require an organic or inorganic electron donor, as well as anoxic conditions to biodegrade ClO_4^- (Coates and Achenbach, 2004), and NO_3^- has been observed to impede biodegradation for many (but not all) ClO_4^- reducing strains (Farhan and Hatzinger, 2009; Chaudhuri et al., 2002). Thus, in aquifers with historically high levels of DO, ORP, and/or NO_3^-, biodegradation of ClO_4^- is unlikely. Similarly, low DOC (as one measure of potential organic electron donor abundance) also will limit biodegradation. Finally, when conditions are correct for ClO_4^- biodegradation, rates of this process are often very rapid and complete (making *in situ* and *ex situ* bioremediation viable treatment approaches; Hatzinger, 2005), unlike the slow kinetics often observed during biodegradation of chlorinated solvents, MTBE, and various other pollutants for which CSIA is applied. Thus, the potential for partially biodegraded and isotopically fractionated ClO_4^- to persist in an aquifer where biodegradation is occurring is less likely than for many other traditionally recalcitrant compounds.

Figure 3.6. Relation b etween $\varepsilon^{18}O$ and $\varepsilon^{37}Cl$ during bacterial reduction of ClO_4^-. The data presented represent results from laboratory studies in which ClO_4^- biodegradation by two strains was measured at two different temperatures (10 °C and 22 °). The isotopic fractionation factor ratio [$\varepsilon^{18}O/\varepsilon^{37}Cl=2.5$] is independent of strain and temperature (figure from Sturchio et al., 2007).
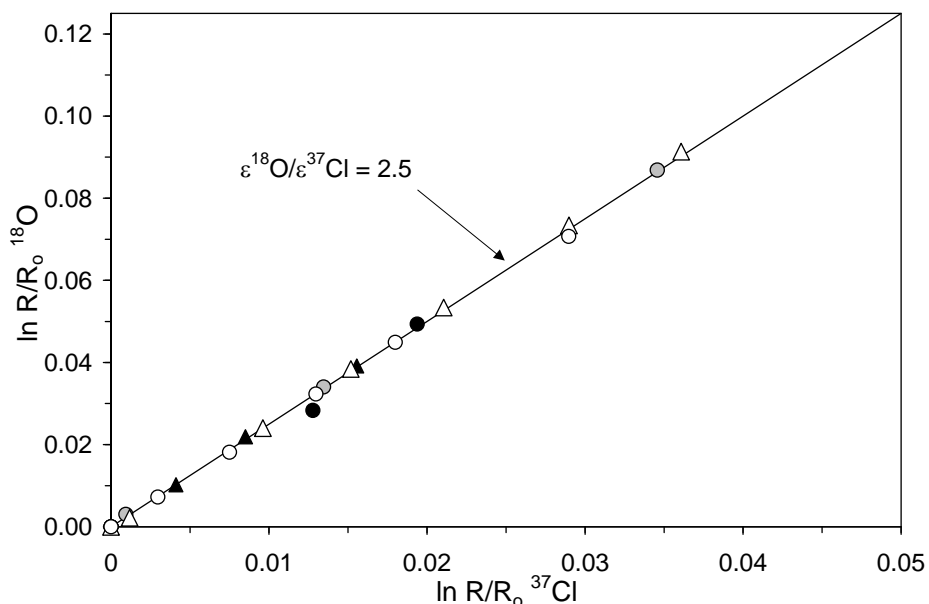
Figure 3.7. Relation between $\delta^{18}O$ and $\delta^{37}Cl$ values of synthetic and Chilean ClO_4^-, isotopic compositions of mixtu res of thes e sources, a nd the isoto pic compositions of residual ClO_4^- during biodegradation. The extent of biodegradation is given by *f*, the residual fraction, assuming $\varepsilon^{18}O=-36.25‰$ and $\varepsilon^{37}Cl=-14.5‰$; $\varepsilon^{18}O/\varepsilon^{37}Cl=2.5$.
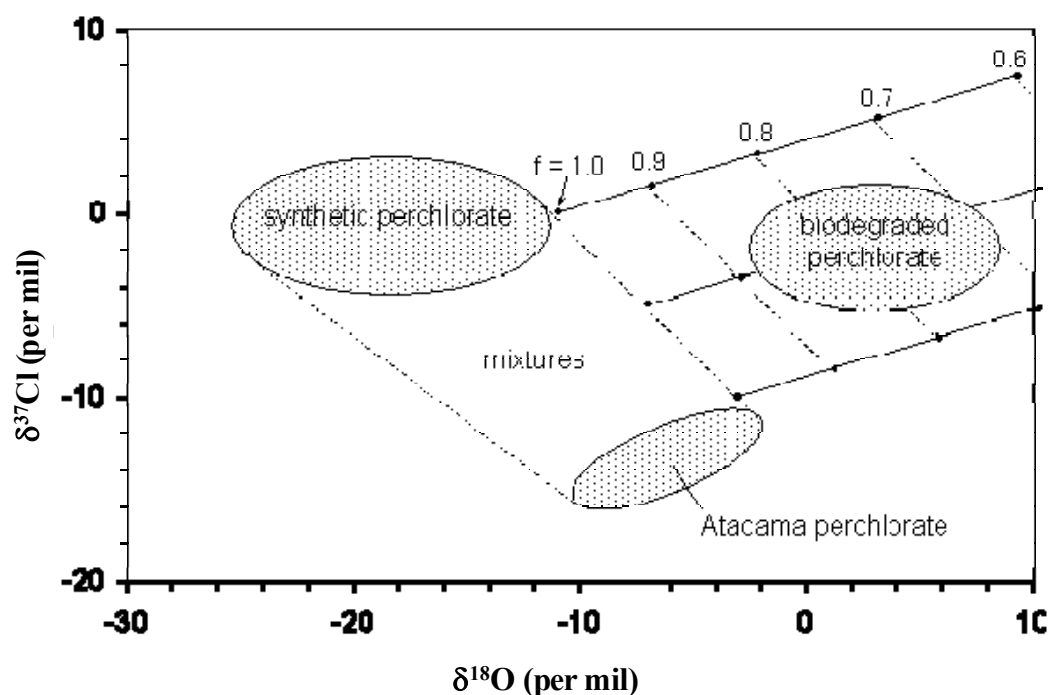
Figure 3.8. Microbial isotopic fracti onation trajectory compared to $\delta^{18}O$ and $\delta^{37}Cl$ values of various ClO_4^- sources. Arrows indicate direction of change for $\varepsilon^{18}O/\varepsilon^{37}Cl=2.5$.
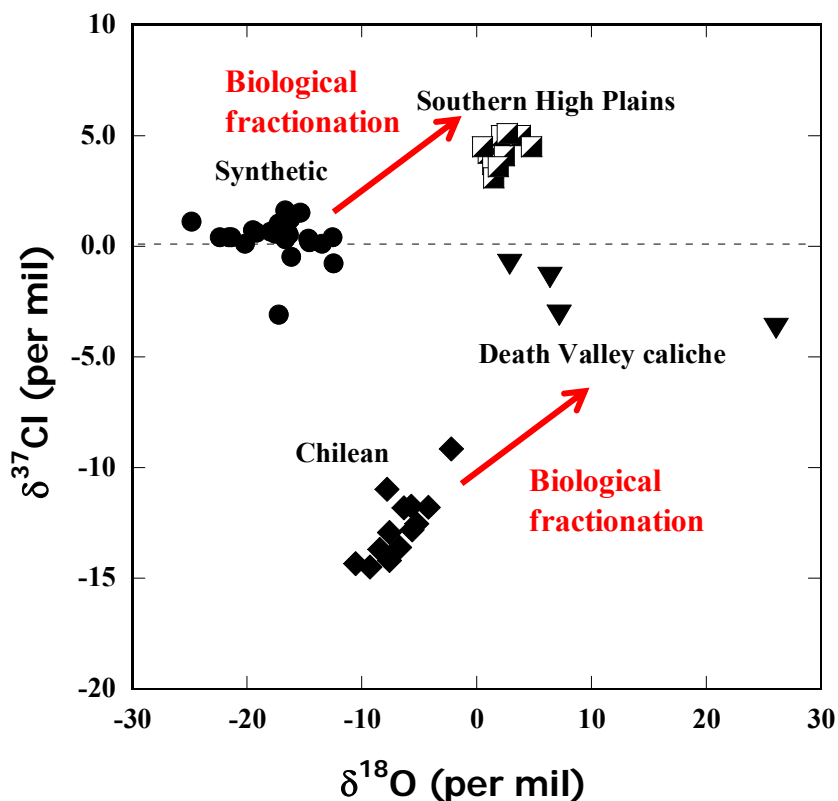
3.4.2 Exchange of Oxygen between Perchlorate and Water

Besides biological isotopic fractionation, exchange of O in ClO_4^- with surrounding H_2O in an aquifer or elsewhere could lead to post depositional changes in the $\delta^{17}O$ and $\delta^{18}O$ values of ClO_4^-. Because Cl is the central atom in ClO_4^- and is bonded to four O molecules, exchange of Cl may be less likely. The USGS has been evaluating the potential for the exchange of O by ClO_4^- in a long-term study. During this evaluation, which is ongoing, ClO_4^- (from perchloric acid [$HClO_4$]) with a known O isotopic composition was mixed with ^{18}O-enriched H_2O ($\delta^{18}O=+156‰$), and the mixture was sealed and incubated at room temperature (22 ± 1 °C). Periodically, subsamples of the solution are removed and the O isotopic composition of the ClO_4^- is measured by IRMS, as described previously. After nearly 5 yr of incubation, evidence for exchange of O between the ^{18}O-enriched H_2O and the ClO_4^- is negligible (Figure 3.9) (Böhlke et al., unpublished data). Based on the current data from this study, the half-life of O isotope exchange between ClO_4^- and H_2O is >4500 yr. These results extend those of a previous investigation indicating minimal exchange of O between ClO_4^- and H_2O, with a half-life of >100 yr (Hoering et al., 1958). Additional studies are ongoing to assess whether biological activity or mineral catalysts can accelerate the exchange reaction, but field data so far indicate that the integrity of the ClO_4^- source O isotopic ratios is maintained over at least several decades under normal groundwater

conditions. This was indicated, for example, by the isotopic composition of known synthetic ClO_4^- near the end of a groundwater flow path with modeled transit time of around 30-50 yr from the source near Henderson, NV (Böhlke et al., 2005). It was indicated also by the detection of ClO_4^- with isotopic composition similar to that of Chilean nitrate fertilizer in groundwater on Long Island, NY 20 to 40 yr after the groundwater was recharged (Böhlke et al., 2009), as summarized in Section 4.0.

Figure 3.9. Values of $\delta^{18}O$ in ClO_4^- during long-term incubation in ^{18}O-enriched H_2O.
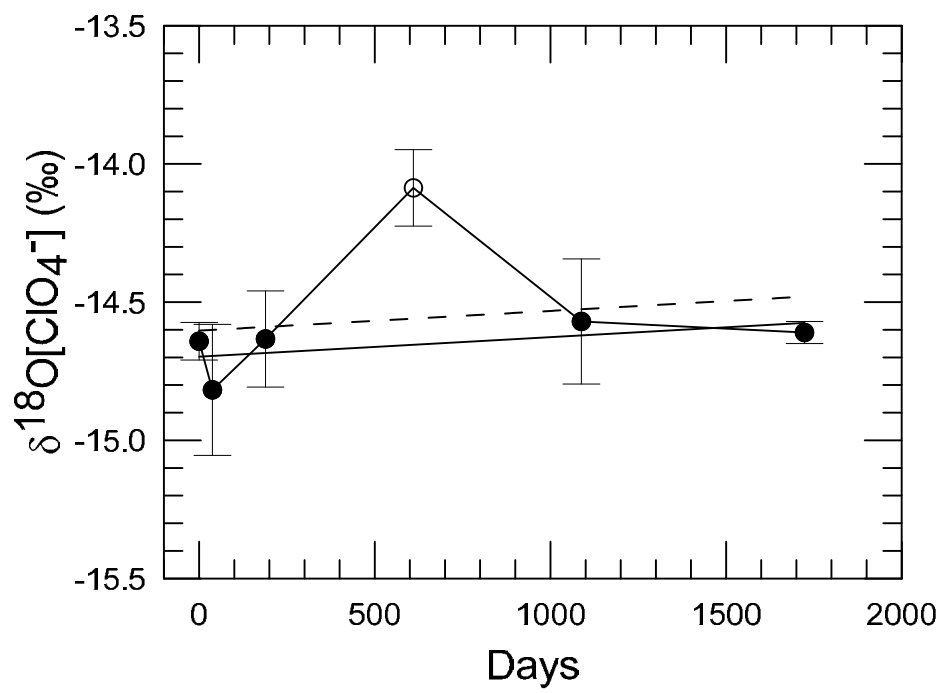
4.0 CASE STUDY OF PERCHLORATE SOURCE IDENTIFICATION: LONG ISLAND, NEW YORK

The information presented in this guidance manual describes three principal ClO_4^- sources that are likely to be found in soils and groundwaters in the United States (i.e., synthetic ClO_4^-, Chilean nitrate fertilizer-derived ClO_4^-, indigenous natural ClO_4^-) and shows that these sources are isotopically distinct when all relative stable isotope ratios of O and Cl (expressed as $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$) are taken into consideration (Bao and Gu, 2004; Böhlke et al., 2005, 2009; Sturchio et al. 2006, 2011; Jackson et al., 2010). The mole fraction of radioactive ^{36}Cl (expressed as $^{36}Cl/Cl$) in the different sources also is a useful distinguishing characteristic (Sturchio et al. 2009). In addition, current results indicate that O exchange between ClO_4^- and H_2O is insignificant in water over at least decades if not centuries, so the isotopic characteristics of source ClO_4^- can be maintained in groundwater, at least on anthropogenic time scales (Böhlke et al., 2005, 2009). Finally, although ClO_4^- is subject to biodegradation under appropriate conditions (i.e., anoxic, low NO_3^-, available electron donor, presence of ClO_4^--reducing bacteria), this process results in predictable stable isotope effects that will not substantially alter $\Delta^{17}O$ or $^{36}Cl/Cl$ values and generally will not cause any one source to be isotopically indistinguishable from another. Thus, even if a source is partially biodegraded, the initial source(s) generally can be determined. Also, evaluation tools exist to determine the likelihood that biodegradation has affected ClO_4^- by examining other chemical indicators in a sample.

Based on these findings, several source-attribution studies involving unknown sources of ClO_4^- have been conducted using stable isotopic analysis, traditional hydrogeological investigations, and many of the supporting geochemical parameters described in Table 2.1. These studies were conducted in Pasadena, CA (Slaten et al., 2010), San Bernardino, CA (Sturchio et al., 2011), Chino, CA (Chino Watermaster, unpublished data), Long Island, NY (Böhlke et al., 2009), and near the Stringfellow Superfund Site in Glen Avon, CA (Hatzinger, 2008). Data from the Stringfellow study, which showed the presence of Chilean fertilizer-derived ClO_4^- in addition to synthetic sources, have been used by the California Department of Toxic Substance Control (DTSC) to explain the distribution of low levels of ClO_4^- in groundwater in some areas of the Stringfellow site. (http://www.dtsc.ca.gov/SiteCleanup/Projects/upload/Stringfellow_FS_Update_0329100.pdf). We are aware of other studies that are currently ongoing but for which there are currently no published data.

One of the previous studies, from Long Island, NY, is summarized below as a case study of the application of the ClO_4^- stable isotope methodology described herein for environmental forensic studies when sources are unknown. The reader is encouraged to review the published papers for additional details on this study, as well as others noted above that are not included in this document.

4.1 CHARACTERISTICS OF SITES AND WELLS

The objective of this forensic evaluation was to assess probable sources of ClO_4^- in groundwater at multiple locations within Suffolk County on Long Island, NY. The full details are presented in Böhlke et al. (2009). Perchlorate has been detected in groundwater in numerous locations on Long Island, with various sources possible based on current and past activities (Abbene, 2006;

Munster, 2008). These sources include fireworks production and use, agricultural fertilizer application (historical and current), road flares, military facilities including missile launch sites, disinfection with bleach, and others. Groundwater in which ClO_4^- was previously detected was sampled using IX columns, as described in Section 2.2 of this document. The well locations are shown in Figure 4.1. Samples were collected from two production wells in the Northport area of western Suffolk County by placing an IX column on a slipstream from each well, as shown in Figure 4.2. These wells, which are screened 93 ± 10 m and 117 ± 9 m below ground surface (bgs) are within the Magothy aquifer. This region was primarily agricultural in the 1950s, but much of the land is now residential. Samples were also obtained from two shallow groundwater monitoring wells at a former BOMARC (Boeing and Michigan Aerospace Research Center) missile site near Westhampton, New York. This site was deactivated in 1969 and was converted to a training facility for police by Suffolk County. Activities at the site at the time of this study included weapons training and fireworks disposal by open burning in a pit. Both wells were upgradient from the former missile silos and downgradient from a firing range and fireworks disposal pit. Finally, a monitoring well transect was sampled in the North Fork area in the northeast part of Suffolk County (Depot Lane). This transect consisted of three nested monitoring wells running in a northwest-southeast array across the middle of the North Fork Peninsula. Land use in this area is primarily agricultural. These wells are screened within the surficial upper glacial aquifer (Schubert et al., 2004). The deepest well screens are just above a lower confining unit, which begins at approximately -35 to -31 m elevation (Bohn-Buxton et al., 1996).

Figure 4.1. Location map of groundwater wells sampled for ClO_4^- source identification on Long Island, NY (modified from Böhlke et al., 2009).
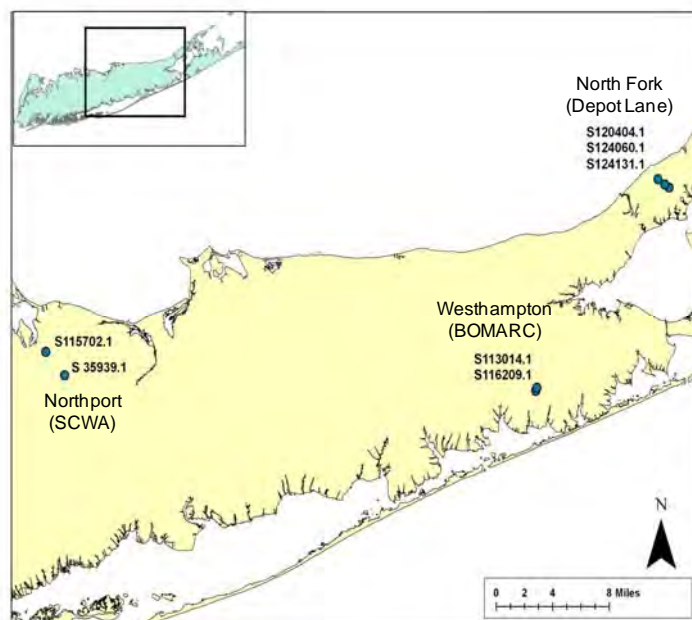
Figure 4.2. Sample collection setup for ClO$_4^-$ from a public supply well on Long Island, NY.

4.2 SAMPLE COLLECTION AND ANALYSES

Groundwater field parameters were measured at each well (DO, pH, conductivity, and temperature) and samples were collected essentially as described in Section 2.8.1 of this document, with supporting parameters as summarized previously in Table 2.1. In addition to IX columns for ClO_4^- collection for Cl and O isotopic analyses, groundwater samples were collected for isotopic analyses of N, S, and O in NO_3^- and SO_4^{2-}, for concentration analyses of ClO_4^-, anions, trace elements,, and major dissolved gases (Ar, N_2, O_2, and CH_4), and for groundwater-age dating (^3H, ^3He, SF_6, and CFCs as described in Section 2.8 and Table 2.1). Samples were obtained between December 2006 and April 2008.

4.3 RESULTS OF CHLORINE AND OXYGEN ISOTOPIC ANALYSES OF PERCHLORATE

Perchlorate was detected at the highest concentrations at the former BOMARC site (~360 to 4300 µg/L), where fireworks disposal and military activities were considered the most likely sources. The Suffolk County production wells had ClO_4^- concentrations of 8.4 to 11.2 µg/L, and the deep nested wells at Depot Lane had concentrations from ~4.6 to 10 µg/L. The shallow nested wells at Depot Lane had concentrations of only 0.2 to 1.0 µg/L, which was too low to permit collection of samples for isotopic analysis using available equipment and site access. The $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values of the ClO_4^- collected from the BOMARC wells (n=2) were consistent with values typical of synthetic ClO_4^-, while samples from the Northport production wells (n=2) and the deep Depot Lane wells (n=3) were consistent with natural ClO_4^- from Chile (Figure 4.3). There was no indication of ClO_4^- biodegradation or denitrification (see Böhlke et al., 2009 for data) in the site groundwater.

The two BOMARC wells, which contained unusually high concentrations of ClO_4^-, were near a fireworks disposal pit. The groundwater in the wells also had anomalously high concentrations of K, Sr, and Sb, as determined by ICP-MS analysis. These elements commonly are used for color and brightness in fireworks (Conklin, 1985). Although various local sources of synthetic ClO_4^- may be present at this site, leaching of unexploded fireworks as the cause of groundwater contamination is supported by presence of a fireworks disposal pit in the area, the extremely high ClO_4^- levels in each of the wells, the anomalously high concentrations of trace elements common to many fireworks, and the young ages of the groundwaters (1 to 2 yr, based on environmental tracer data).

In contrast to the BOMARC wells, the Cl and O isotopic compositions of ClO_4^- from the Depot Lane wells and Northport production wells were consistent with ClO_4^- found in Chilean nitrate deposits and fertilizers. Groundwater in these wells also had relatively high concentrations of NO_3^- and other constituents that are typical of recharge beneath fertilized agricultural land in this region, such as Ca, Mg, and SO_4^{2-} (see Böhlke et al., 2009 for data and further explanation). No other ClO_4^- sources, including the U.S. indigenous sources, are currently known to have the distinctive combination of low $\delta^{37}Cl$, low $\delta^{18}O$, and high $\Delta^{17}O$ values that characterize the Chilean ClO_4^-. Thus, the data indicate that the ClO_4^- in these wells was derived from the historical use of Chilean nitrate fertilizers on Long Island. Age dating of groundwater supports this hypothesis (see Section 4.4 and Figure 4.4B). It is apparent from the data that the distinctive Cl and O isotopic compositions of the Chilean ClO_4^- were not altered substantially by O

exchange or other plant, soil, or mineral reactions during transport and aging in the Long Island aquifers.

Figure 4.3. Comparison of $\delta^{37}Cl$ **versus** $\delta^{18}O$ **(Plot A) and** $\Delta^{17}O$ **versus** $\delta^{18}O$ **(Plot B) in** ClO_4^- **from wells on Long Island with those of synthetic and Chilean source materials.** The data from the Long Island wells are plotted as black diamonds, the data from synthetic sources as open red circles, and those from Chilean samples as open blue squares.
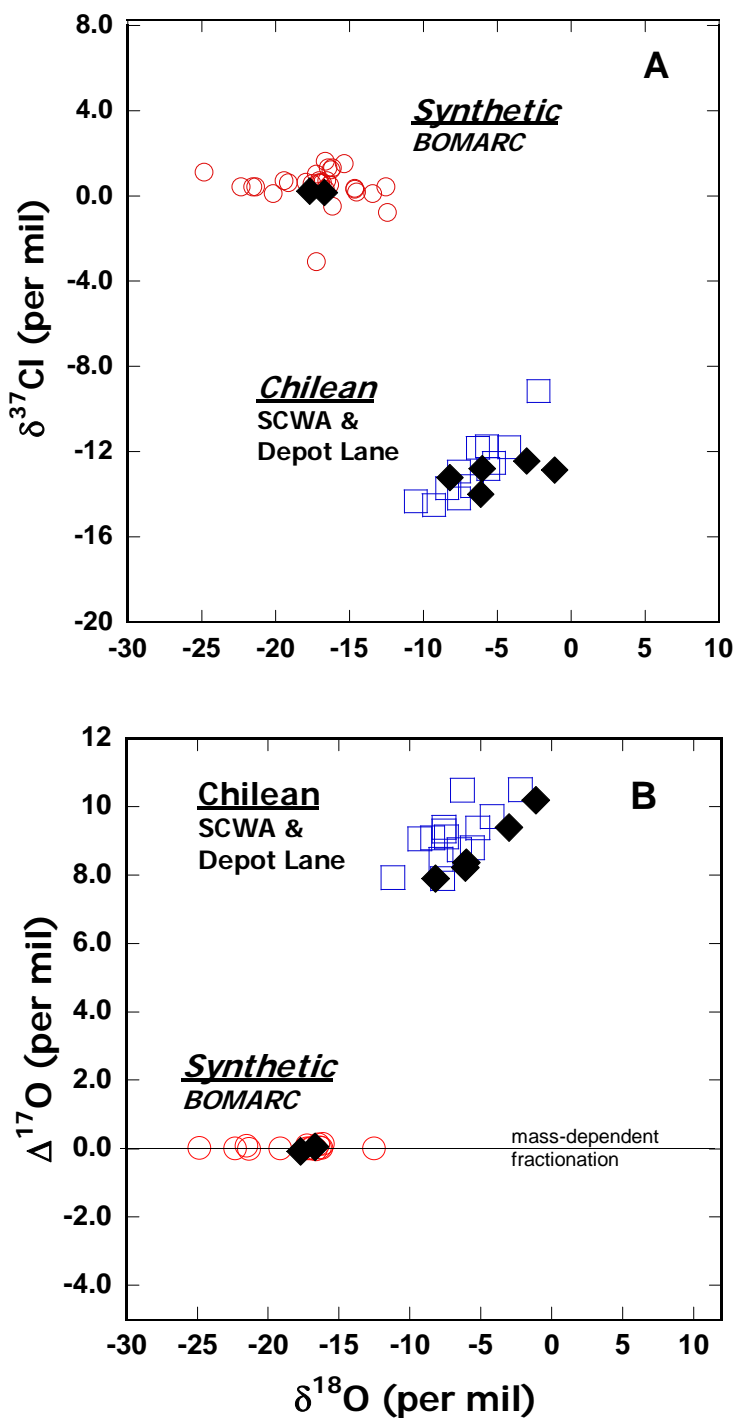
4.4 GROUNDWATER-AGE DATING AND OTHER SUPPORTING DATA

Groundwater-age dating provided valuable information during this study. Apparent recharge dates and ages of groundwater (time in saturated zone after recharge) were estimated from concentrations of various atmospheric tracers including ^{3}H-^{3}He, SF_6, and CFCs, as summarized in Böhlke et al. (2009). Based on the tracer data, a composite mean apparent age was estimated for groundwater in each well, and the results ranged from ~1 to 41 yr with uncertainties of the order of 2 to 5 yr. The groundwater in the BOMARC wells was recharged within the previous 2 yr prior to groundwater sample collection. The presence of recently recharged water is consistent with fireworks from the disposal pit area as a source of ClO_4^- contamination. At the North Fork (Depot Lane) transect wells, apparent groundwater ages ranged from ~1 to 39 yr and increased with depth as did the mean concentration of ClO_4^-, while the relatively high levels of NO_3^- remained almost constant with groundwater depth and age (Figure 4.4).

The consistently lower ClO_4^- concentrations in younger groundwater, with the relatively constant NO_3^-, were interpreted by Böhlke et al. (2009) to reflect changing agricultural practices, with quantities of ClO_4^- bearing Chilean fertilizer declining and being replaced by other sources without ClO_4^- over the past several decades (possibly including low-ClO_4^- Chilean fertilizer in recent years). This groundwater trend (decreasing ClO_4^- and constant or slightly increasing NO_3^-) resembles qualitatively the overall patterns of Chilean and non-Chilean fertilizer use in the United States since the mid-1900s (Figure 4.5). This interpretation is also consistent with Chilean ClO_4^- as a source in the Northport area production wells, as the composite apparent groundwater ages at these wells were 35 and 41 yr, respectively, similar to those of the deeper wells in the Depot Lane transect that had Chilean ClO_4^-. These groundwaters apparently recharged when land use was more agricultural than at present. Data from several other locations sampled during ESTCP Project ER-200509, including sites in North Carolina, New Jersey, and several locations in California, indicate that Chilean ClO_4^- may be common in aerobic aquifers that underlie regions with an agricultural history that included applications of imported Chilean nitrate fertilizer.

4.5 SUMMARY OF LONG ISLAND PERCHLORATE SOURCE STUDY
The stable isotope results (δ^{37}Cl, δ^{18}O, and Δ^{17}O) for ClO_4^- and key supporting chemical and environmental tracer data collected from several wells on Long Island provide strong evidence for the presence of ClO_4^- derived from Chilean nitrate fertilizer as well as that from a synthetic source, presumably fireworks disposal. The groundwater at all locations was aerobic and undenitrified, and ClO_4^- apparently was not affected isotopically by biodegradation or exchange processes in the subsurface. In an agricultural region, ClO_4^- concentrations and the ratio of ClO_4^-/NO_3^- increased with increasing groundwater age (from ~1 to 40 yr based on atmospheric tracers), most likely as a result of declining application rates of Chilean nitrate fertilizer. Stable Cl and O isotopic analyses of ClO_4^- indicates that past use of imported Chilean nitrate fertilizer on Long Island has led to legacy contamination of some aquifer units, even though this fertilizer may have been applied in relatively small quantities as long as 40 or more years ago.

Figure 4.4. Vertical distribution of NO$_3$-N and ClO$_4^-$ concentrations in nested wells along a transect in the North Fork area of Long Island. The estimated time since recharge of the groundwater at different depths in the DL 4 well nest is also given. Figure modified from Böhlke et al. (2009).
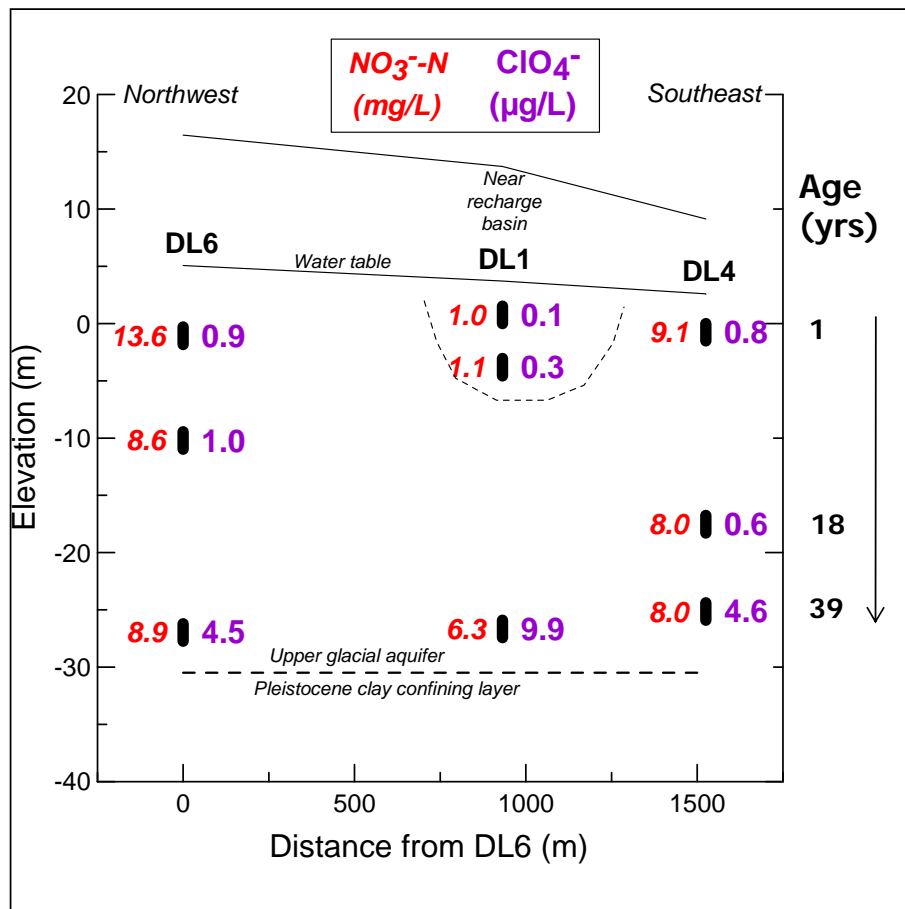
Figure 4.5. National trends of Chilean fertilizer use (Atacama NO$_3^-$) and total N fertilizer use in the United States (modified from Böhlke et al., 2009).
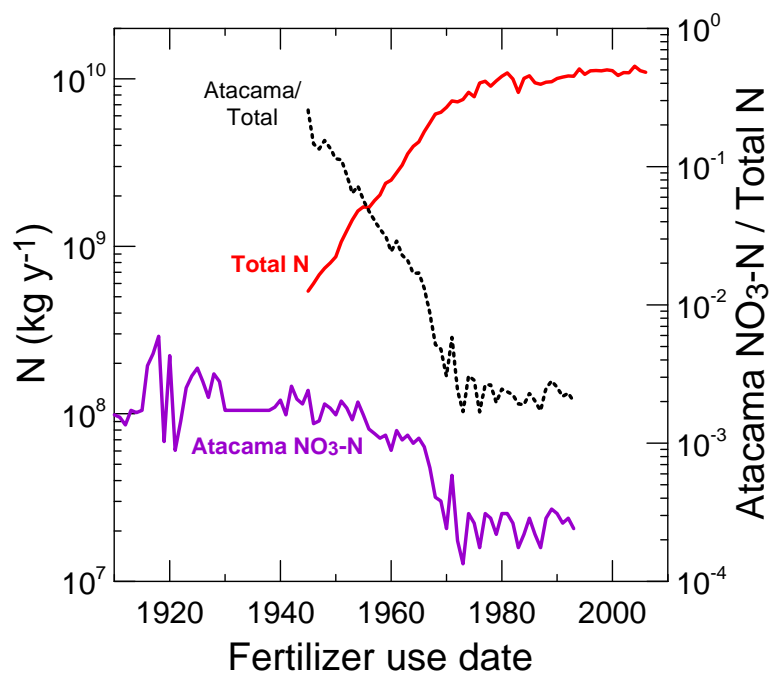
5.0 SUMMARY AND CONCLUSIONS

The key objective of this document is to describe isotopic techniques that can be used to discern the origin of ClO_4^- in soils and groundwater, and more specifically whether that ClO_4^- is synthetic or natural. These techniques determine the relative abundances of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- using IRMS and the radioactive isotope ^{36}Cl using AMS. Taken together, these measurements on the ClO_4^- ion (which provide four independent quantities) can be used to distinguish natural from synthetic ClO_4^- sources, to discriminate different types of natural ClO_4^-, and to detect ClO_4^- biodegradation in the environment. Other isotopic, chemical, and hydrogeologic techniques that can be applied in conjunction with the Cl and O isotopic analyses of ClO_4^- to provide supporting data for forensic studies are also described.

The key points presented in this document are as follows:

1. Perchlorate (ClO_4^-) has both synthetic and natural sources, each of which contributes to its occurrence in soils and groundwater. Typical analytical methods for determining ClO_4^- concentrations do not provide direct information on its potential origin.

2. A new forensic approach for ClO_4^- has been developed, based on measurements of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O), and a radioactive chlorine isotope (^{36}Cl) in ClO_4^-. The basic steps in this approach are as follows:

   - Sample collection using ion exchange (IX) columns to trap mg quantities of ClO_4^- from groundwater or soil extracts
   - Extraction and purification of ClO_4^- from IX columns
   - Verification of sample purity via Raman spectroscopy and/or ion chromatography
   - Analysis of stable O isotopes in ClO_4^- by IRMS
   - Analysis of stable Cl isotopes in ClO_4^- by IRMS
   - Analysis of ^{36}Cl by AMS.

3. The data gained from these isotopic analyses can be used to distinguish natural from synthetic ClO_4^- in both source materials and environmental samples. Key isotopic characteristics of different types of ClO_4^- are as follows, based on current published results (see Appendix A):

   - Synthetic ClO_4^- produced by electrochemical reaction is characterized by a mean $\delta^{37}Cl$ value (with respect to SMOC) of 0.6‰ and exhibits little variation among samples (-3.1 to +1.6‰), more variable $\delta^{18}O$ values (with respect to VSMOW) ranging from -24.8 to -12.5‰, and $\Delta^{17}O$ values near 0‰, consistent with mass-dependent isotopic fractionation of O during ClO_4^- synthesis. This material also is characterized by low $^{36}Cl/Cl$ values (^{36}Cl mole fractions) of 0×10^{-15} to 40×10^{-15}.
   - Natural ClO_4^- from caliche deposits in the Atacama Desert of Chile, and nitrate fertilizers derived from this material, have reported $\delta^{37}Cl$ values ranging from -14.5‰ to -11.8‰, with a mean value more than 10‰ lower than that of synthetic ClO_4^-. Reported $\delta^{18}O$ values of Atacama ClO_4^- (-24.8‰ to -4.2‰) exhibit substantial overlap with the $\delta^{18}O$

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values of synthetic ClO_4^-, but the Atacama ClO_4^- is characterized by substantially elevated values of $\Delta^{17}O$ (+4.2 to +9.6‰), indicating non-mass-dependent isotope effects or precursors contributed to its formation, most likely during atmospheric generation. This natural ClO_4^- has slightly elevated $^{36}Cl/Cl$ values (22×10^{-15} to 590×10^{-15}) compared to synthetic ClO_4^-.

- Natural ClO_4^- from the southwestern United States varies somewhat by location and environment. Samples collected from a large area of the Southern High Plains (SHP) and the Middle Rio Grande Basin (MRGB) are similar isotopically, with $\delta^{37}Cl$ values ranging from +3.1 to +5.0‰, $\delta^{18}O$ values ranging from +0.6 to +3.8‰, and $\Delta^{17}O$ values ranging from +0.3 to +1.3‰. These data indicate that ClO_4^- from the SHP and MRGB is distinguishable from both Chilean ClO_4^- and synthetic ClO_4^- when all relevant stable isotope ratios are considered.

- Natural ClO_4^- samples from caliche deposits in and around Death Valley, CA, have lower $\delta^{37}Cl$ values (-0.8 to -3.7‰) and much higher $\Delta^{17}O$ values (+ 8.6 to +18.4‰) compared to the SHP and MRGB samples. Interestingly, however, all of the SHP, MRGB, and Death Valley samples analyzed to date are characterized by substantially elevated $^{36}Cl/Cl$ values (3130×10^{-15} to $28,800 \times 10^{-15}$) compared to those of synthetic or Chilean ClO_4^-. Overall, the SHP, MRGB, and Death Valley samples can be considered together as U.S. indigenous sources and, even though there are substantial ranges in the individual isotope ratios, this indigenous grouping is isotopically distinct from synthetic and Chilean ClO_4^- when all relevant isotope ratios are considered.

4. Experiments to date indicate that post depositional modification by biodegradation causes a reproducible fractionation factor ratio between O and Cl isotopes in ClO_4^- ($\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$) that is roughly perpendicular to the area in which mixtures of synthetic and Chilean ClO_4^- plot in dual isotope plots. Thus, biodegradation will not obscure differences between these two major sources, when considered with the large differences in $^{36}Cl/Cl$ and(or) $\Delta^{17}O$ values (which will not change appreciably during biodegradation). Biodegradation is also unlikely to lead to lead to errors in source delineation among indigenous U.S. sources and synthetic or Chilean sources of ClO_4^- when all relevant parameters are considered.

5. In addition to Cl and O isotopes of ClO_4^-, there are a large number of supporting methods/analyses available as forensic lines of evidence to help identify sources of ClO_4^- (or other contaminants) in a groundwater environment. These analyses include basic field parameters; stable H, O, N, and S isotopes in H_2O, NO_3^-; and SO_4^{2-}, concentrations of anions, dissolved gases, and trace elements; and groundwater-age dating. The use of these methods in conjunction with Cl and O isotopic analyses of ClO_4^- is recommended in studies to identify the origin of ClO_4^- in groundwater.

6. The currently defined ranges of isotopic compositions characteristic of different ClO_4^- sources may evolve as more samples are analyzed, but these data already have proven useful for identifying perchlorate sources in a number of groundwater studies and we expect additional data will enhance the value of this approach for ClO_4^- forensic applications.

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Commercial analysis of Cl and O isotopes in ClO_4^- is conducted by EIGL under the supervision of Dr. Neil Sturchio. To our knowledge, no other facilities currently offer this analysis on a commercial basis.

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APPENDIX A: STABLE ISOTOPE DATA FOR PERCHLORATE SOURCES

TABLE A-1. CHLORINE AND OXYGEN ISOTOPIC COMPOSITIONS OF PERCHLORATE SOURCE SAMPLES

Sample Identification	ClO_4 Salt	Sample Description	$\delta^{37}Cl$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)
SYNTHETIC					
Laboratory Reagents	$NaClO_4$	Mallinckrodt lot # 1190KHJJ[1]	+1.2	-16.2	+0.01
	$KClO_4$	Baker Analyzed lot # 45155[1]	+1.1	-24.8	+0.01
	$NaClO_4 \cdot H_2O$	Aldrich lot # 00722CG[1]	+1.3	-16.1	+0.12
	$KClO_4$	Sigma lot # 60K3451[1]	+0.5	-16.3	n.a.[4]
	$NaClO_4$	Sigma lot # 111K1334[1]	+1.0	-17.6	n.a.
	$KClO_4$	Hummel-Croton[1]	+0.4	-12.5	n.a.
	$NaClO_4 \cdot H_2O$	EM lot # SX0693-2[1]	-3.1	-17.2	+0.08
	$KClO_4$	General Chem. Co. lot # 13[1]	+0.6	-19.1	+0.00
	$RbClO_4$	Aldrich lot # AN00625LZ[1]	+1.3	-16.4	+0.11
	$CsClO_4$	Aldrich lot # LI09119JI[1]	+1.6	-16.6	-0.04
	$CsClO_4$	Aldrich lot # 02407AS[1]	+0.6	-16.9	+0.00
	$HClO_4$	Baker 9656-1, lot # 146358[1]	n.a.	-14.6	+0.01
	$KClO_4$	Aldrich, lot # 11921HO[1]	+0.6	-17.0	+0.00
	$KClO_4$	Allied Chemicals[2]	n.a.	-19.9	-0.06
	$KClO_4$	Aldrich[2]	n.a.	-17.8	-0.12
	$NaClO_4$	EM-Science[2]	n.a.	-17.3	-0.06
	$NaClO_4$	Fisher Scientific[2]	n.a.	-19.5	-0.20
	$AgClO_4$	Aldrich[2]	n.a.	-17.3	-0.10
Manufactured ClO_4^-	$NaClO_4$	American Pacific Co. (N3300401)[1]	+0.4	-22.3	-0.01
	$KClO_4$	American Pacific Co. (P0900402)[1]	+0.4	-21.5	+0.07
	NH_4ClO_4	American Pacific Co. (A2000433)[1]	+0.4	-21.3	n.a.
	$NaClO_3$	Western Electrochemical Co. (TO403E)[1]	+1.1	n.a.	+0.06
	$NaClO_4$	Western Electrochemical Co. (TO403B)[1]	+0.9	-20.4	+0.00
NATURAL					
Chilean ClO_4^-	$KClO_4$	Commercial Hoffman fertilizer[1]	-13.7	-8.4	+8.95
	$CsClO_4$	Commercial Hoffman fertilizer[1]	-14.5	-9.3	+8.93
	$CsClO_4$	Atacama, Chile evaporite (AT-74-1)[1]	-11.8	-4.2	+9.57
	$CsClO_4$	SQM-7791 fertilizer (RSIL N7791)[1]	-14.2	-7.6	+9.25
	$CsClO_4$	Atacama (AT-24-1)[2]	n.a.	-4.6	+9.6
	$CsClO_4$	Atacama (AT-74-1)[2]	n.a.	-4.5	+9.6

	KClO$_4$	Atacama (AT-75-1)[2]	n.a.	-24.8	+4.2
	CsClO$_4$	Commercial Hoffman fertilizer[2]	n.a.	-9.0	+8.8
Chilean *ClO$_4$ (Con't)*	CsClO$_4$	Atacama – well water[3]	-12.9	-7.6	+9.3
	CsClO$_4$	P1[3]	-14.3	-10.5	+8.1
	CsClO$_4$	P2[3]	-13.6	-6.7	+9.2
	CsClO$_4$	P3[3]	-11.8	-5.7	+8.8
	CsClO$_4$	P4[3]	n.a.	-7.8	+8.5
	CsClO$_4$	GJ01[3]	-12.5	-5.2	+9.4
	CsClO$_4$	J-470[3]	-12.5	-5.6	+8.8
Southern High Plains	CsClO$_4$	Well - MW2A[3]	+4.2	+1.0	+0.3
Groundwater	CsClO$_4$	Well - MW2B[3]	+3.7	+1.4	+0.3
	NaClO$_4$	Well - MW3A[3]	+5.0	+2.2	+0.3
	CsClO$_4$	Well - MW3B[3]	+4.1	+2.4	+0.3
	CsClO$_4$	Well - GW2[3]	+5.0	+3.8	+0.2
	CsClO$_4$	Well - BW2[3]	+4.5	+0.6	+0.6
	NaClO$_4$	Well - JTY1[3]	+5.1	+2.7	+0.5
	HClO$_4$	Well - KJ1[3]	+4.5	+4.8	+0.8
	CsClO$_4$	Well - RR-8[3]	+3.1	+1.5	+1.2
	CsClO$_4$	Well - RR 16[3]	+3.6	+1.9	+1.3
	CsClO$_4$	Well TTU-G1S[1]	+6.2	+4.7	+0.4
	CsClO$_4$	Well TTU-M3L[1]	+5.1	+2.5	+0.5
Southern High Plains					
Vadose Zone		SHP-V[3]	+3.7	+2.1	+0.8
Death Valley Caliche	CsClO$_4$	Confidence Hills 1[3]	-0.8	+2.9	+8.6
	CsClO$_4$	Confidence Hills 2[3]	-3.8	+7.2	+12.8
	CsClO$_4$	Saratoga Hills[3]	-1.4	+6.4	+10.9
	CsClO$_4$	Zabriskie[3]	-3.7	+26.1	+18.4

[1] Data from Sturchio et al. (2006)
[2] Data from Bao and Gu (2004)
[3] Data from Jackson et al. (2010)
[4] n.a. - data "not available"

APPENDIX B: OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT AS OF APRIL, 2003 (MAYER, 2003)

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
AL	Redstone Army Arsenal - NASA Marshall Space Flight Huntsville, AL	Propellant Manufacturing, Testing, Research, Disposal	Monitoring Well Springs/Seeps	19,000 37
AL	Unregulated Contaminant Monitoring Rule (UCMR) data Escambia County, AL	Unknown	Public Water Supply	8.9
AZ	Apache Nitrogen Products Benson, AZ	Explosives Manufacturing	Monitoring Well	670
AZ	Aerodyne Gila River Ind. Res., Chandler, AZ	Propellant Testing	Monitoring Well	18
AZ	Davis Monthan AFB Tucson, AZ	Explosives/ Propellant Disposal	Soil	--
AZ	Unidynamics Phoenix Inc. Phoenix Goodyear Airport Goodyear, AZ	Explosives/Ordnance Manufacturing	Public Water Supply Well Monitoring Well	65 80
AZ	Unidynamics Phoenix Inc. White Tanks Disposal Area Maricopa County, AZ	Explosives/ Ordnance Disposal	Soil	--
AZ	Universal Propulsion Phoenix, AZ	Rocket Manufacturing	Soil	--
AR	Atlantic Research East Camden, AR	Rocket Manufacturing Disposal- Open burn/ Open detonation	Monitoring Well Surface Water Soil	640,000 12,500 --
CA	Aerojet General Rancho Cordova, CA	Rocket Manufacturing	Public Water Supply Well Monitoring Well	260 640,000
CA	Alpha Explosives Lincoln, CA	Explosives Manufacturing	Monitoring Well Reported in Surface Water	67,000
CA	Boeing/ Rocketdyne, NASA at Santa Susana Field Lab USDOE Santa Susana, CA	Rocket Research, Testing and Production	Monitoring Well	750
CA	Casmalia Resources Casmalia, CA	Hazardous Waste Management Facility	Monitoring Well	58
CA	El Toro Marine Corps Air Station Orange County, CA	Explosives Disposal	Monitoring Well	380
CA	Edwards AFB Jet Propulsion Lab, North Base Edwards, CA	Rocket Research	Monitoring Well	300

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil Disposal Area concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE
RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc ppb
CA	Lawrence Livermore National Laboratory Site 300 Tracy, CA	U.S. Dept. of Energy Explosives Research	Monitoring Well	84
CA	Lockheed Propulsion Upper Santa Ana Valley Redlands, CA	Rocket Manufacturing	Public Water Supply Well	87
CA	NASA - Jet Propulsion Lab Pasadena, CA	Rocket Research	Public Water Supply Well	54
CA	Olin Safety Flare Site Morgan Hill, CA	Flare Manufacturing	Public Water Supply Well Monitoring Well	15 167
CA	Rancho Cordova Test (Affects Mather AFB) Rancho Cordova, CA	Boeing/ McDonnell Douglas Rocket Testing	Public Water Supply Well Monitoring Well	120 1800
CA	Rialto-Colton Plume Rialto, CA	Fireworks Facility Flare Manufacturing Rocket Research and Manufacturing	Public Water Supply Well	811
CA	San Fernando Valley Glendale, CA	Grand Central Rocket ? Rocket Manufacturing	Monitoring Well	13
CA	San Gabriel Valley Baldwin Park, CA	Aerojet Rocket Manufacturing	Public Water Supply Well Monitoring Well	159 2,180
CA	San Nicholas Island Ventura County, CA	U.S. Navy Firing Range	Public Water Supply (Springs)	12
CA	Stringfellow Superfund Site Glen Avon, CA	Hazardous Waste Disposal Facility	Monitoring Well Private Well	682,000 37
CA	UTC (United Technologies) San Jose, CA	Rocket Testing	Monitoring Well	180,000
CA	Whittaker-Bermite Ordnance Santa Clarita, CA	Ordnance Manufacturing	Public Water Supply Well	47
CA	Whittaker Ordinance Hollister, CA	Ordnance Manufacturing	Private Well Monitoring Well	810 88
CO	Pueblo Chemical Depot Pueblo, CO	Munition Demobilizing Open burn/ Open detonation	Monitoring Well	180
GA	Unregulated Contaminant Monitoring Rule (UCMR) data Houston County, GA	Unknown	Public Water Supply	5.2
GA	Unregulated Contaminant Monitoring Rule (UCMR) data Oconee County, GA	Unknown	Public Water Supply	38

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003 [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
IA	Ewart, IA	Unknown source	Livestock Well	29
IA	Hills, IA	Unknown source	Private Well	30
IA	Iowa Army Ammunition Plant Middleton, IA	Propellant handling	Monitoring Well	9
IA	Napier, IA	Agriculture(?)	Private Well	11
KS	Herington, KS	Ammunition Facility	Monitoring Well	9
MD	Aberdeen Proving Grounds Aberdeen, MD	Field Training - Pyrotechnics and Explosives	Public Water Supply Well Monitoring Well/ Hydropunch	5 24
MD	Naval Surface Warfare Center Indian Head, MD	Propellant Handling	Waste Discharge to Surface Water	>1,000
MD	White Oak Fed. Research Center (Naval Surface Warfare Center) White Oak, MD	Propellant Handling	Monitoring Well/ Hydropunch	798
MD	Unregulated Contaminant Monitoring Rule (UCMR) data Hagerstown, MD	Unknown - Open burn/	Public Water Supply	4
MA	Massachusetts Military Res. Barnstable County, MA	Disposal Open detonation	Monitoring Well	100
MN	Unregulated Contaminant Monitoring Rule (UCMR) data New Brighton, MN	Unknown	Public Water Supply	4.5
MN	Unregulated Contaminant Monitoring Rule (UCMR) data Northfield, MN	Unknown	Public Water Supply	6
MO	ICI Explosives Joplin, MO	Explosives Facility	Monitoring Well	107,000
MO	Lake City Army Amm. Plant Independence, MO	Propellant Handling	Monitoring Well	70
NE	Lewiston, NE	Agricultural Chemical Facility	Shallow Private Well	5
NE	Mead, NE	Fireworks Facility	Monitoring Well	24
NV	Boeing/Rocketdyne near Reno, NV	Propellant Testing	Monitoring Well	400
NV	Kerr-McGee/BMI Henderson, NV	Perchlorate Manufacturing	Public Water Supply Monitoring Well Surface Water	24 3,700,000 120,000
NV	PEPCON Henderson, NV	Perchlorate Manufacturing	Monitoring Well	600,000

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE
RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
NJ	Unregulated Contaminant Monitoring Rule (UCMR) data Middlesex County, NJ	Unknown	Public Water Supply	7
NJ	Picatinny Arsenal Morris County, NJ	Munitions Handling	Monitoring Well	627
NM	Cannon AFB Clovis, NM	Explosives Disposal	Public Water Supply	46
NM	New Mexico American Water Co Clovis, NM	Unknown	Public Water Supply Well	5.8
NM	Deming, NM	Agricultural	Public Water Supply Well	20
NM	Des Moines, NM	Agricultural	Public Water Supply Well	4.5
NM	Fort Wingate Depot Activity Gallup, NM	Explosives Disposal	Monitoring Well Soil	2,860 --
NM	Holloman AFB Alamogordo, NM	Rocket Testing	Monitoring Well Seasonal Surface Water Soil	40 16,000 --
NM	Los Alamos National Lab Los Alamos, NM	U.S. Dept of Energy Lab Chemicals	Public Water Supply Well Monitoring Well Deep Borehole Water	3 220 1,662
NM	Melrose Air Force Range Melrose, NM	Explosives	Public Water Supply Well	40.7
NM	Mountain View Albuquerque South Valley, NM	Agricultural	Public Water Supply Well	4.8
NM	White Sands Missile Range White Sands, NM	Rocket Testing	Monitoring Well Soil	21,000 --
NY	Unregulated Contaminant Monitoring Rule (UCMR) data Bethpage, NY	Unknown	Public Water Supply	5
NY	Unregulated Contaminant Monitoring Rule (UCMR) data Plainview, NY	Unknown	Public Water Supply	11
NY	Westhampton Suffolk County, NY	Unknown Source(s), Possibly Agricultural	Public Water Supply Well Monitoring Well	16 3,370
NY	Yaphank Suffolk County, NY	Fireworks	Private Well Monitoring Well	26 122
NC	Unregulated Contaminant Monitoring Rule (UCMR) data Nash County, NC	Unknown	Public Water Supply	5.8
OR	Umatilla Army Depot, Ammunition Demolition Activity Hermiston, OR	Munitions Disposal OB/OD	Monitoring Well	10

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE
RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
OR	Elf Atochem Portland, OR	Perchlorate Manufacturing	Monitoring Well	1000
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Berks County, PA	Unknown	Public Water Supply	4
PA	Unregulated Contaminant County, PA Monitoring Rule (UCMR) data Crawford	Unknown	Public Water Supply	33
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Huntingdon County, PA	Unknown	Public Water Supply	6.7
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Lancaster County, PA	Unknown	Public Water Supply	12
TX	Andrews County, TX	Unknown Source(s)	Public Water Supply Well	15.8
TX	Dawson County, TX	Unknown Source(s)	Public Water Supply Well Private Well	26 58.8
TX	Ector County, TX	Unknown Source(s)	Public Water Supply Well	5
TX	Gaines County, TX	Unknown Source(s)	Public Water Supply Well Private Well	27 30
TX	Glasscock County, TX	Unknown Source(s)	Public Water Supply Well Private Well	1.1* 3* *estimated
TX	Howard County, TX	Unknown Source(s)	Public Water Supply Well Private Well	1.4* 26 *estimated
TX	Unregulated Contaminant Monitoring Rule (UCMR) data Kleburg County, TX	Unknown Source	Public Water Supply Well	4.5
TX	Unregulated Contaminant Monitoring Rule (UCMR) data Hockley County, TX	(s)Improper Cathodic Protection	Elevated Storage Tank	32
TX	Lone Star Army Ammunition Plant Texarkana, TX	Propellant and Munitions Handling	Monitoring Well Surface Water Soil	23 6 --
TX	Longhorn Army Ammunition Depot Karnak, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	169,000 -- --
TX	Martin County, TX	Unknown Source(s)	Public Water Supply Well Private Well	32 19.1

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
TX	McGregor Naval Weapons Plant McGregor, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	91,000 — --
TX	Midland County, TX	Unknown Source(s)	Public Water Supply Well	46
TX	PANTEX Plant (USDOE) Amarillo, TX	Explosives	Monitoring Well	340
TX	Red River Army Depot Texarkana, TX	Propellant Handling	Monitoring Well	80
UT	Alliant Tech Systems Magna, UT	Rocket Manufacturing	Public Water Supply Well	16
UT	Thiokol Promontory, UT	Rocket Manufacturing	Water Supply Well (Inactive)	42
VA	Unregulated Contaminant Monitoring Rule (UCMR) data Accomack County, VA	Unknown	Public Water Supply	4.3
WA	Camp Bonneville near Vancouver, WA	Explosives/Propellant OB/OD Disposal	Monitoring Wells	200
WA	Unregulated Contaminant Monitoring Rule (UCMR) data Lakewood, Pierce County, WA	Unknown	Public Water Supply	6
WA	Unregulated Contaminant Monitoring Rule (UCMR) data Puyallup, Pierce County, WA	Unknown	Public Water Supply	8
WV	Allegheny Ballistics Lab Rocket Center, WV	Rocket Research, Production, OB/OD	Surface Discharge of Groundwater Extraction	400

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.